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DESIGN GUIDELINES FOR USE OF ADHESIVES AND ORGANIC COATINGS IN HYBRID MICROCIRCUITS

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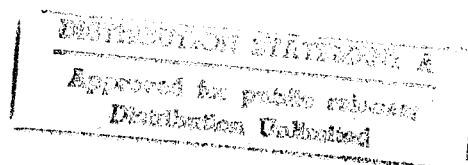
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16. ABSTRACT

A study was conducted to investigate the reliability of organic adhesives in hybrid microcircuits. The objectives of this study were twofold: (1) to identify and investigate problem areas that could result from the use of organic adhesives and (2) to develop evaluation tests to quantify the extent to which these problems occur for commercially available adhesives. Efforts were focused on electrically conductive adhesives. Also, a study was made to evaluate selected organic coatings for contamination protection for hybrid microcircuits. The results of these studies are reported.

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DESIGN GUIDELINES FOR USE OF ADHESIVES AND ORGANIC COATINGS IN HYBRID MICROCIRCUITS

INTRODUCTION

Until recently, most discrete electronic components have been electrically and mechanically connected into package assemblies using solder bonding techniques. Today's complex semiconductor microcircuits, ceramic components, and other leadless devices possess physical and chemical characteristics which are adversely affected by high-temperature solder and eutectic processes. Therefore, organic materials are being used in microelectronic applications as a replacement for the metallurgical techniques. These uses include adhesive bonding of components for mechanical, electrical and thermal purposes; package sealing; substrate mounting, and other applications.

The use of adhesives in lieu of eutectic bonding or other metallurgical attachment is highly desirable from both a reliability and manufacturing process standpoint. Organic adhesives can be processed and cured at lower temperatures (usually below 150°C); allow easy rework, removal, and replacement of components without subjecting the circuits to high temperatures, and, because of their low moduli of elasticity, allow stress dissipation without damaging the component, bond line, or substrate. This latter property is particularly important during temperature cycling or thermal shocking of circuits, especially in the case of larger components such as capacitors. Previous investigations have clearly delineated that solder-joined capacitors are susceptible to catastrophic failures during temperature cycling, and, consequently, it has been recommended that this assembly technique not be used for meeting the requirements of high-reliability microcircuits.

MICROELECTRONIC PACKAGING

Assembly Techniques

In recent years, more and more electronics hardware has been designed into smaller packages. Not only are these subassemblies made smaller, but generally they perform more electronic functions. Microelectronics, in

addition to reduced weight and size, consume less power and are more reliable than the discrete counterpart. The standard printed circuit board, when used, contains discrete components with wire leads. These leads are soldered or welded into place on the board to form mechanical and electrical connections as shown in Figure 1.
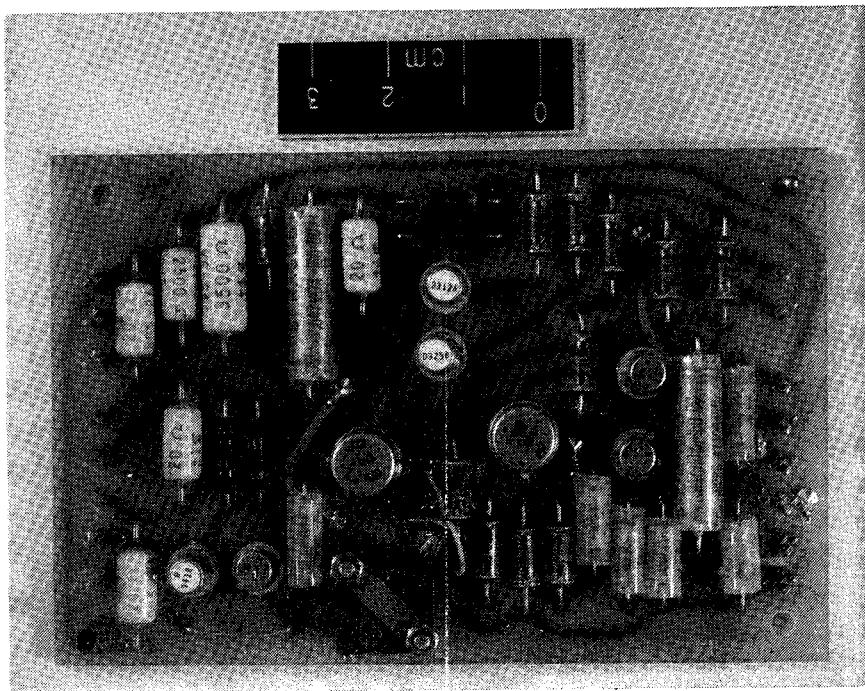
Figure 1. Conventional printed circuit board with leaded components.

In comparison with printed circuit board assembly, greater packaging densities can be achieved with discrete monolithic integrated circuits and hybrid microcircuit assemblies as illustrated in Figure 2. As seen in this illustration, discrete components must be mounted onto the base substrate using new bonding techniques because of the leadless configurations. A comparison is shown in Figure 3 of the component configurations used in printed circuit boards as contrasted with the devices that are generally used in microcircuit integrated packaging. The obvious difference is the fact that the devices used in high-density microcircuit packages generally do not have leads preattached, as is the case with conventional resistors, capacitors, etc. Therefore, new mounting techniques have been developed for use with this technology.

FLAT PACK

"T.O." CAN AND LID
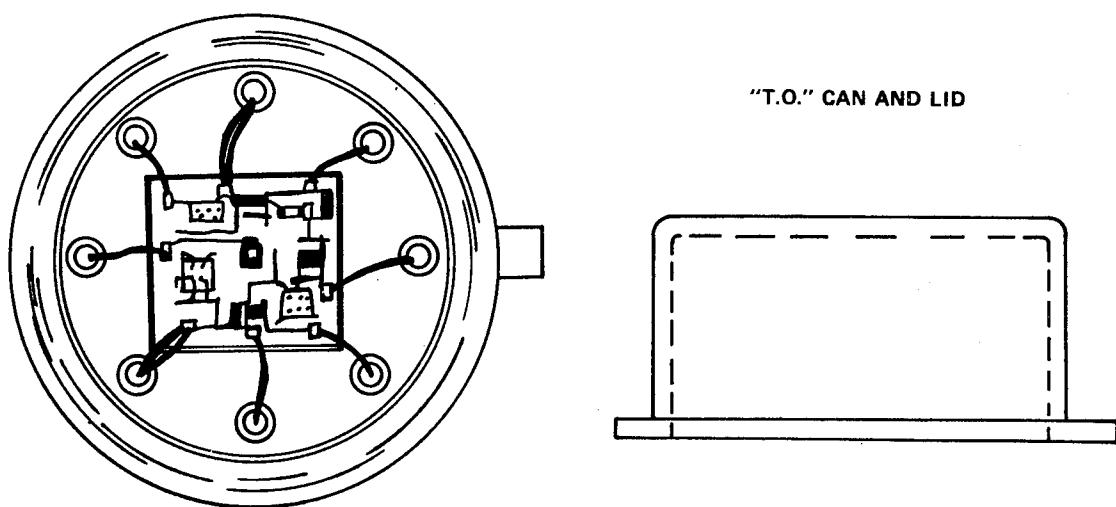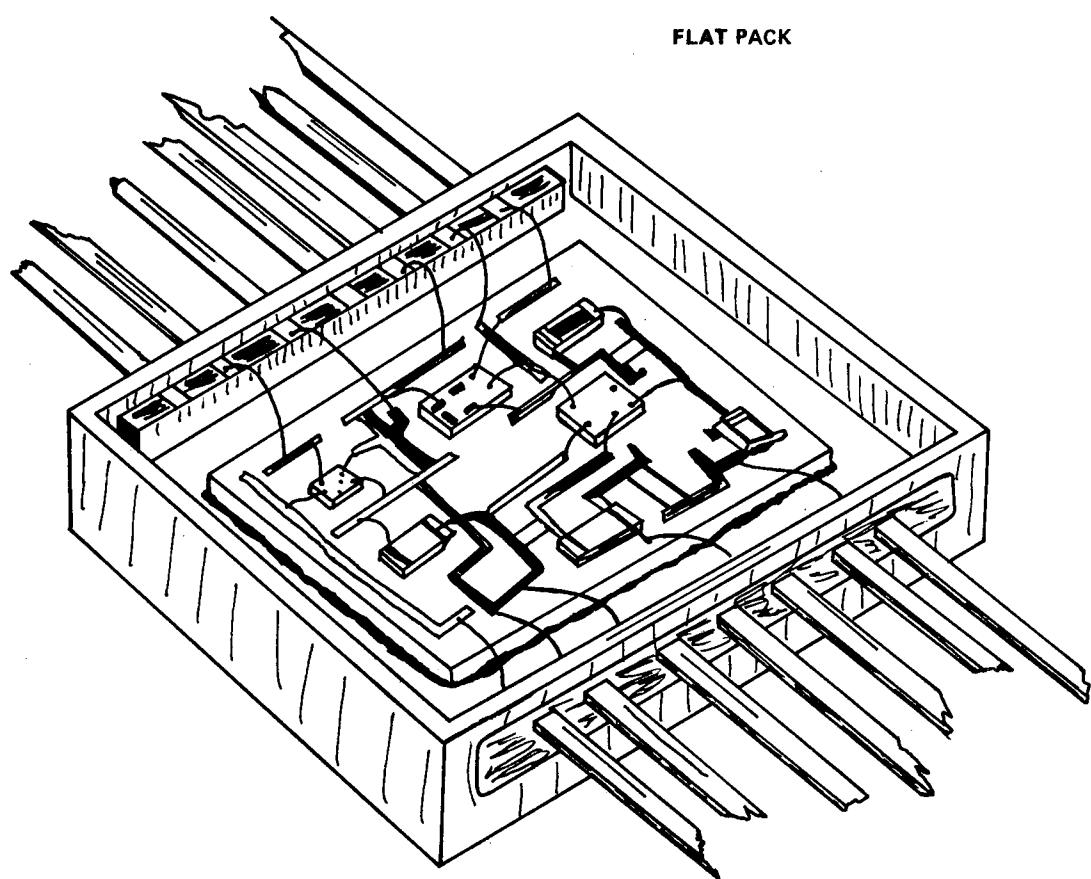
Figure 2.   Monolithic and hybrid integrated circuit
packaging technology.
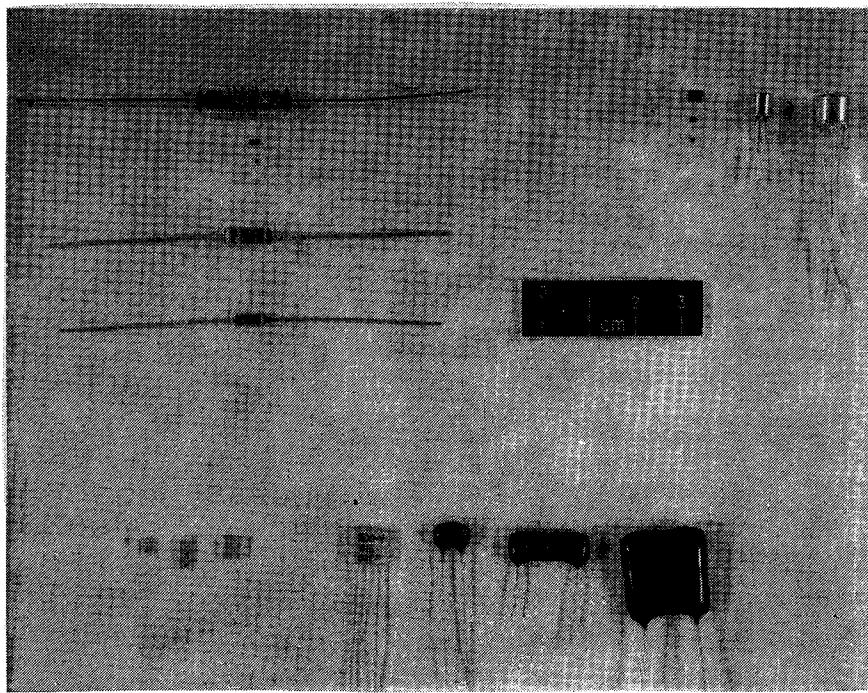
Figure 3. Comparison of discrete devices for printed circuit
boards and hybrid microcircuits.

Device Mounting Technology

The fact that modern integrated microcircuits are constructed with
leadless devices has caused problems in mounting these components. Standard
metallurgical processes and materials such as solders, eutectic bonding, and
reflow brazing have been and are currently being used; however, these tech-
niques have a number of disadvantages which adversely affect the reliability of
the entire circuit. Primarily, with metal attachment techniques, the compo-
nents are held rigidly to the substrate (usually ceramic), as shown in Figure 4.
A ceramic chip capacitor is shown soldered in place on a ceramic substrate.
Because of the difference in material properties such as the thermal coefficient
of expansion (TCE), temperature cycling causes stress that can result in
damage to the component, substrate and/or bond line.

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CAPACITORS

SOLDER OR CONDUCTIVE
EPOXY MOUNTED

EPOXIED TO SUBSTRATE,
AND WIRE BONDED

CHIP RESISTORS

CHIP EPOXIED TO SUBSTRATE,
AND WIRE BONDED

SOLDER MOUNTED

INTEGRATED CIRCUIT CHIP

SUBSTRATE MOUNTED IN
FLAT PACK
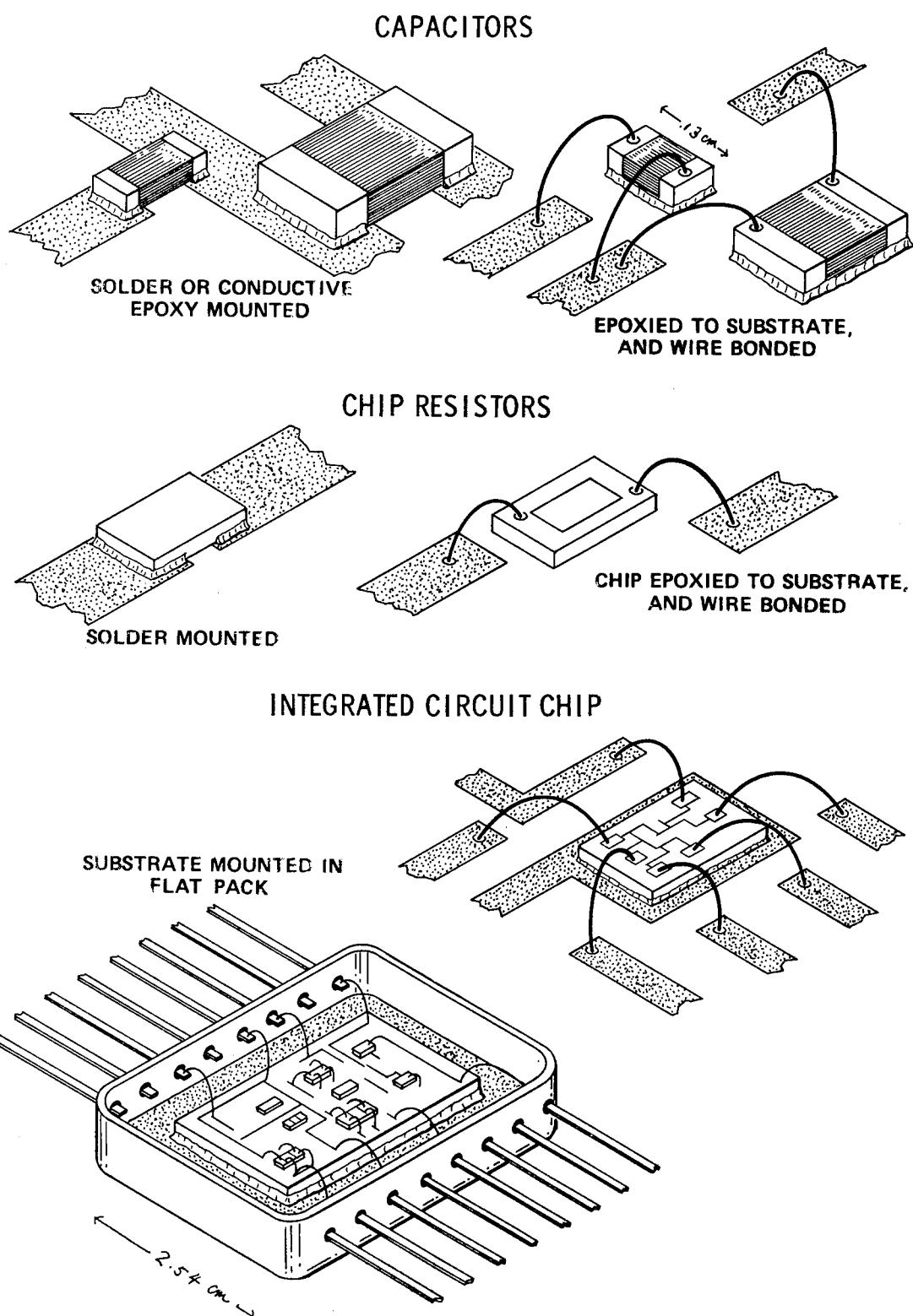
Figure 4. Discrete electronic components used in hybrid packaging technology.

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New Techniques

One relatively new and somewhat controversial development in micro-electronic packaging is the use of organic adhesives in place of metallic materials for discrete component mounting. The advantages of using adhesives, as mentioned previously, are (1) organic adhesives can be processed and cured at low temperatures, (2) they allow easy rework, removal, and replacement of components without subjecting the entire circuit to high temperature, (3) they allow stress dissipation without damaging the component, bond line or substrate, and (4) they can be used as electrically insulative, electrically conductive, and thermally conductive. A method of component attachment is shown in Figure 5.

CAPACITOR
METALIZED
END-CAP

SUBSTRATE
CONDUCTOR
METALIZATION

CERAMIC
CHIP
CAPACITOR

SOLDER
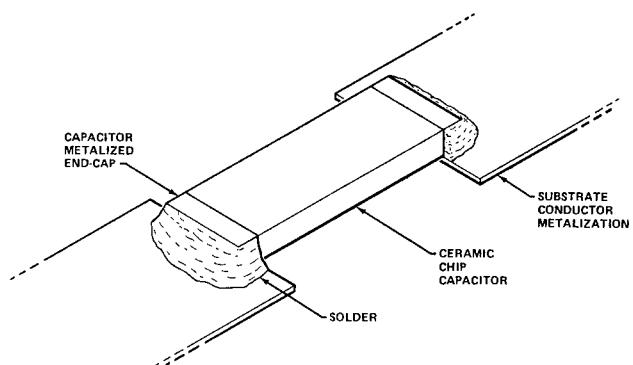
Figure 5. Conventional capacitor attachment method.

SCOPE OF THE STUDY

This study consisted essentially of three efforts: continuing the evaluation of electrically insulative adhesives, performing a similar evaluation of selected electrically conductive adhesives and conducting a preliminary

evaluation of organic materials to assess their suitability for use as protective coatings for hybrid microcircuits. A discussion of the specific tasks constituting these efforts and the results obtained is contained in this report.

ADHESIVES FOR HYBRID MICROCIRCUITS

A discussion of adhesives was given in NASA TM X-64789.* This discussion included enumeration and comments on the properties of organic adhesives considered to be important in determining their suitability for use in hybrid microcircuits, a general review of polymeric types of adhesives, and identification of the major types of adhesives commercially available and specifically designed for microelectronic use.

PROTECTIVE COATINGS FOR HYBRID MICROCIRCUITS

Important Properties for Microcircuit Use

The properties of organic materials that are important in determining their suitability for use as protective coatings for hybrid microcurcuits include those listed and briefly discussed as follows:

Chemical Inertness — Must not react with or cause corrosion on metallization, circuit components, etc.

Purity — Must not contain ions which could cause electrical leakage, insulation breakdown, electrolytic corrosion, or affect device electrical parameters.

Chemical Stability — Must not release volatiles or low molecular weight fractions which could cause corrosion or contamination of circuit components or of adjacent bonding pads and impair further processing; or after cure, must not release volatiles exceeding specified NASA limits.

Thermal Stability — Must not degrade, soften (or harden beyond desired resilience), revert, or decompose at elevated temperatures (or after prolonged exposure to them) and consequently impair mechanical or electrical properties. Must meet NASA outgassing requirements at elevated temperatures after cure. Must not craze or crack at low temperatures.

_____

* S. V. Caruso, J. J. Licari, and K. L. Perkins: Design Guidelines for Use of Adhesives in Hybrid Microcircuits, July 1973.

Film Integrity — Coating film must be pinhole-free, complete, and continuous to ensure that the total circuit is protected.

Compliancy — Must be easily molded or readily conforming and not create stresses during cure.

Shrinkage — Shrinkage during cure must not be such as to excessively stress circuit components, etc., or to impair the integrity of the coating.

Acceptable Cure Schedule — Not greater than 150°C.

Electrical Stability — Must retain adequate electrical properties such as insulation resistance, breakdown voltage, and dielectric constant at elevated temperatures and after prolonged exposure to elevated temperatures.

Application — Must be easily uniformly applied to a reasonably controllable thickness using standard laboratory equipment.

Adhesion — Must adhere to a variety of materials including substrate, circuit components, conductors, etc., and must retain adhesion under the temperature and mechanical test environments of MIL-STD-883.

Resiliency — Must not create excessive mechanical stresses on the circuit components, and must retain coating integrity during the thermal shock and temperature cycling test environments of MIL-STD-883.

Reworkability — Must allow easy removal and replacement of circuit components.

Solvent Resistance — Must be resistant to solvents required for cleaning during processing.

Particle Holding Strength — Must have adequate cohesive strength to hold particles even at elevated temperatures and under vibration test and mechanical shock and constant acceleration test environments of MIL-STD-883.

Hardness — Must be adequately hard to prevent external contaminants from penetrating and contaminating surface and to allow handling during further processing or testing prior to lidding.

Candidate Coating Materials

Generally, a wide variety of commercially available materials can be used as coatings. However, consideration of the properties just listed as important for protective coatings for hybrid microcircuits reduces this number to just four different types: high-purity silicones, polyimides, sputtered Teflon, and p-polyxylenes (Parylenes). A brief discussion of each type follows.

High-Purity Silicones. A number of silicone coatings are commercially available which have been specifically developed as high-purity semiconductor junction coatings. Materials are available in a wide variety of types, ranging from very soft (almost gel-like) to hard and from solvent-based to 100-percent solids.

Of particular interest to this study are the high-purity heat curing types which are polymerized by thermal curing without the release of water or other by-products. In a typical polymerization mechanism, an dichlorobenzoyl peroxide catalyst dissociates into two free-radical molecules which couple to form cross-linkages and are regenerated to repeat the process. Two typical silicone polymerization products are shown in Figure 6.
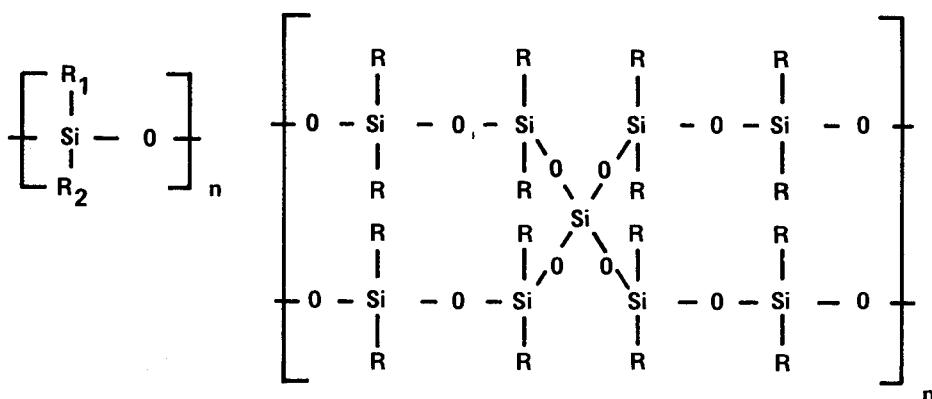
Figure 6. Typical silicone polymerization products.

Although most of the silicone coatings have been ascertained to be of extremely high purity (e.g., less than 1 ppm sodium or heavy metals), they do vary in properties which are critical with respect to device performance under stress. For example, they vary in hardness, and hardness changes with temperature. This characteristic is critical during thermal shock or temperature cycling. The combination of hardness and thermal mismatch can result in mechanical damage.

Several types of silicones have previously been tested at Rockwell International for selected material characteristics. Their performance on specific semiconductor devices has been evaluated under different conditions of environmental and electrical stresses. The results have generally ranged from good to excellent, depending on the severity of the stresses and the type of device.

Polyimides. The polyimides are a relatively new class of polymers distinguished by their very high temperature stability. Continuous service at temperatures of 315 to 370°C (600 to 700°F) and at peak temperatures up to 480°C (900°F) for 5 to 10 min have been reported. The electrical parameters are also very stable over this temperature range.

Polyimides are formed by the condensation of a diamine with an acid dianhydride, first producing an intermediate polyamic acid which, after further curing, condenses to a polyimide. A typical formulation is that of pyromellitic dianhydride and bis (4 aminophenyl)-ether (Fig. 7).

A current commercially available polyimide is PYRE-ML (DuPont). This material has been investigated at Rockwell International as the principal dielectric in a novel multilayer board technology under Contract NAS8-21477 (NASA/MSFC) entitled "Investigation of Multilayer Printed Circuit Board Materials." In this program it was shown that: (1) PYRE-ML can be applied to substrates in several ways, one of the most convenient being a spin-on technique, (2) the films so formed adhered to a variety of substrates and were essentially pinhole-free, (3) the polymer possessed excellent thermal, chemical, and electrical stability and (4) the polymer was completely inert to and compatible with the metals and ceramics normally used in microelectronic packaging.

Sputtered Teflon. It is recognized that fluorinated polymers such as Teflon TFE and Teflon FEP (the chemical structures of which are represented in Figure 8) have a potential for the protection and passivation of uncased semiconductor devices and hybrid thin-film circuits. The Teflons were unique in this respect because of their purity, inertness, high temperature stability, low moisture permeability, and excellent electrical insulation. Previous work which involved Teflon dispersion coatings tested on thin-film array circuits was promising, but the temperatures required to fuse the coatings (300°C to 370°C) were much too high for nichrome resistors and caused resistance changes.

PYROMELLITIC
DIANHYDRIDE

BIS (4-AMINOPHENYL)-ETHER

POLYAMIC ACID

$+H_2O$

POLYIMIDE

$+ H_2O$
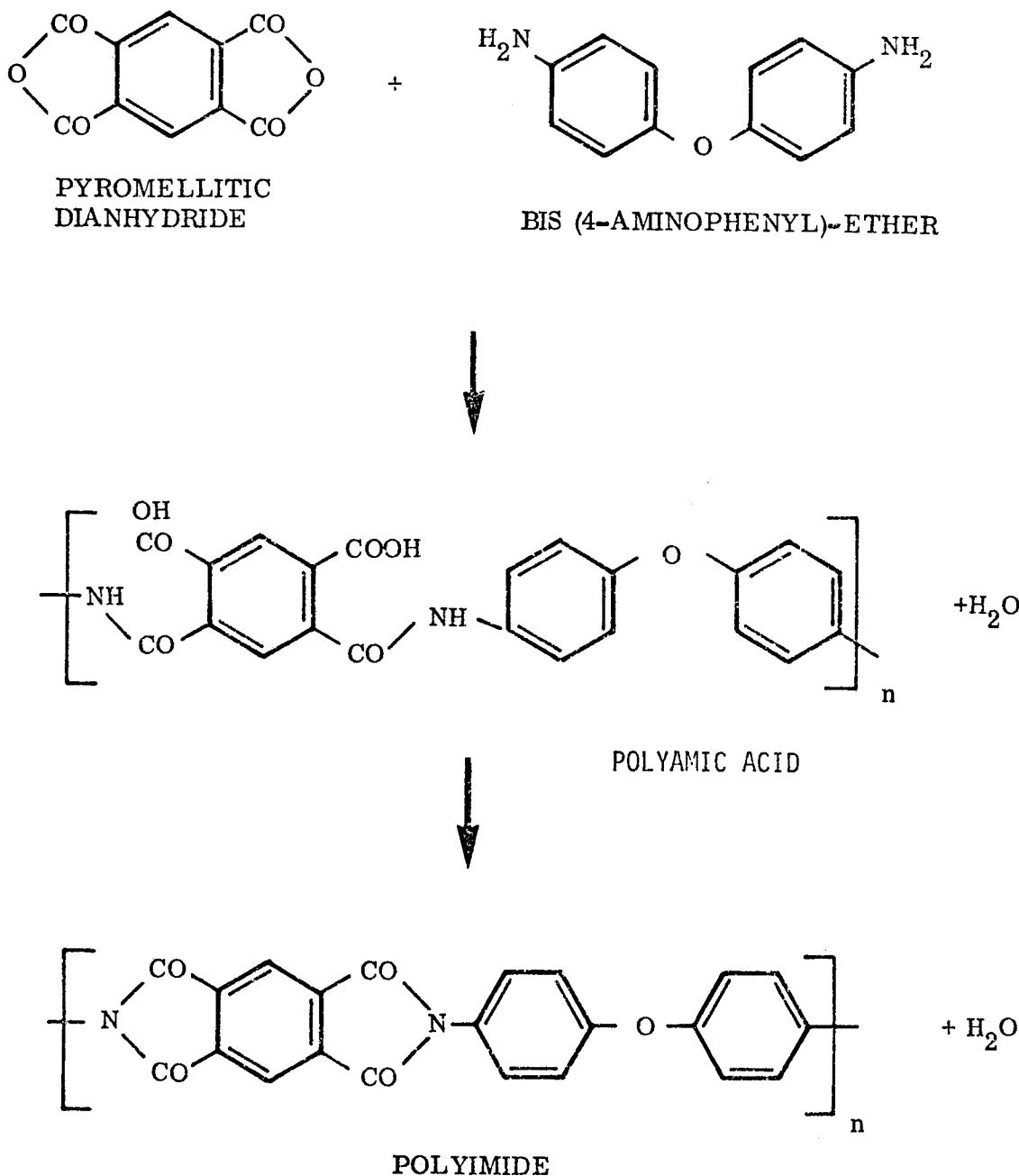
Figure 7. Typical polyimide formation.

$$\left[CF_2 - CF_2 \right]_n$$

Teflon TFE

$$\left[CF_2 - CF_2 - \underset{\underset{CF_3}{|}}{CF} - CF_2 \right]_n$$

Teflon FEP
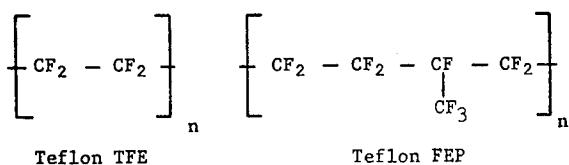
Figure 8. Chemical structures of fluorocarbons.

Recently this problem has been resolved by applying Teflon via the sputtering process in the same way that many metals are deposited. By this process, Teflon can be uniformly deposited while the circuit never gets hotter than 80°C. The process consists of energizing argon gas in an RF discharge at a potential of 1000 to 2000 V so that argon cations are generated. These cations are then accelerated towards a cathodic target which is fabricated from Teflon. The highly accelerated and energetic argon ions impinge on the target and cause Teflon molecules to be dislodged (sputtered off) and redeposited on the substrate to be coated.

Parylenes. Parylene coatings are of interest because of their high purity and complete continuity (absence of pinholes). These coatings can be formed by the pyrolytic dehydrogenation of p-xylene to produce a quinoid p-xylylene, which converts to a highly reactive gaseous biradical monomer. This biradical monomer condenses immediately on contact with a solid surface and continues to build a polymer chain structure as long as a monomer is supplied. In practice, it is more convenient to start with a dimer (available from Union Carbide) which is easily dissociated into the required monomer. The essential reactions are shown in Figure 9.

Because of the method of formation of Parylene, complete and uniform coverage is achieved and no by-products or corrosive contaminants are possible. The films formed are pure, inert (chemically and electrically), pinhole-free, and durable with a controllable thickness range of from 100 nm (1000 Å) up to approximately 70 μm.

It has been shown that Parylene provides an adequate moisture barrier for semiconductor devices under nominal humidity conditions and prevents bi-metallic corrosion of certain very active metal combinations involving steel, magnesium, or aluminum. However, in spite of these very attractive properties, it has been proved that at 150°C and above, Parylene undergoes oxidation and after many hours becomes hard and brittle and no longer is an unbroken film. This temperature limitation may prevent its usage because of MIL-STD-883 burn-in and aging requirements. Other limitations to its wider use on hybrids include its limited availability (exclusive under licensing by Union Carbide) and the difficulty in reworking (at present no practical method is known).
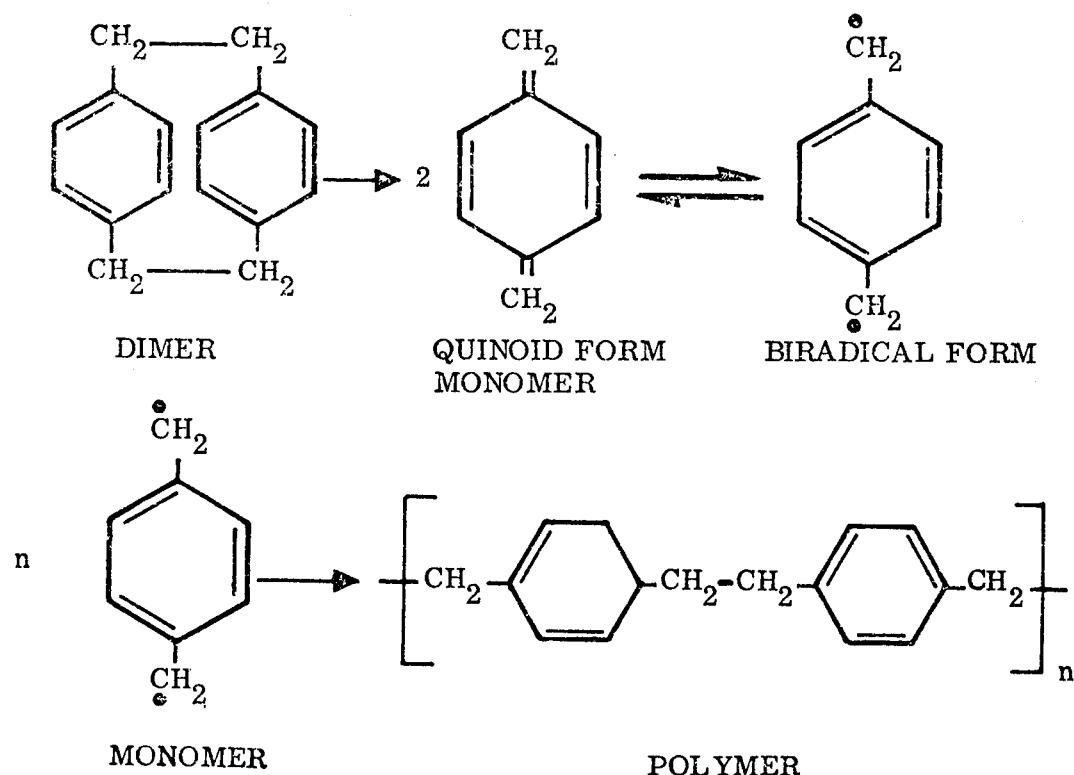
Figure 9. Parylene formation.

ADHESIVES EVALUATION

The evaluation of electrically insulative adhesives begun under a previous study has been continued and a similar evaluation of electrically conductive adhesives has been performed. Briefly, the specific tasks performed were:

1. Bond strength measurements were made for electrically conductive adhesives under the same conditions previously used for electrically insulative adhesives. However, because it was previously shown that bond strengths were not affected by the glaze condition of the surface and because unglazed alumina substrates are now most widely used, standardization has been made on unglazed substrates.

2. Long-term outgassing after cure was determined for electrically conductive adhesives using the breakseal tube method previously described for evaluating electrically insulative adhesives (NASA TM X-64789).

3. Corrosivity tests were run at from 80 to 85°C/80- to 85-percent relative humidity conditions for both electrically insulative and electrically conductive adhesives. Similar tests at from 80 to 85°C/100-percent relative humidity had been run for the electrically insulative adhesives but were not repeated for the electrically conductive adhesives. The 100-percent relative humidity exposure is now considered too severe even as an accelerated test for hermetically sealed hybrids.

4. Weight-loss measurements were made for both electrically insulative and electrically conductive adhesives. These measurements consisted of weight loss during cure and weight loss during programmed temperature rise from 400 to 500°C. In addition, measurements of weight loss after cure were made for two adhesives using the thermal gravimetric analysis (TGA) equipment at a constant temperature of 150°C. Runs were made for approximately 2 hr.

5. Tests were made to evaluate the comparative reliability of using electrically insulative and electrically conductive adhesives to bond chip capacitors.

6. A preliminary guideline specification for the selection and use of organic adhesives for high reliability hybrid microcircuits has been prepared.

Each of these preceding tasks, with the exception of item 6, are discussed in detail on the following pages.

Bond Strength

Bond strength test specimens consisted of ten 0.127- by 0.127-cm (0.050- by 0.050-in.) silicon die bonded to unglazed 1.90- by 3.81-cm (0.75- by 1.50-in.) alumina substrates using the selected electrically conductive adhesives. Adhesive application and die placement were done manually. To ensure that the bond line thickness was relatively uniform for all adhesives, a substrate was notched to a depth of approximately 0.005 to 0.0075 cm (2 to 3 mils) and used to remove the excess adhesive. A photograph of a typical specimen is given in Figure 10. Bond strength measurements were made using the tester (Fig. 11) previously used to test the electrically insulative adhesives. This tester has a 4000-gm capability or 2.43×10^7 N/m^2 or 3530 psi for the 0.127- by 0.127-cm (0.050- by 0.050-in.) die being used.
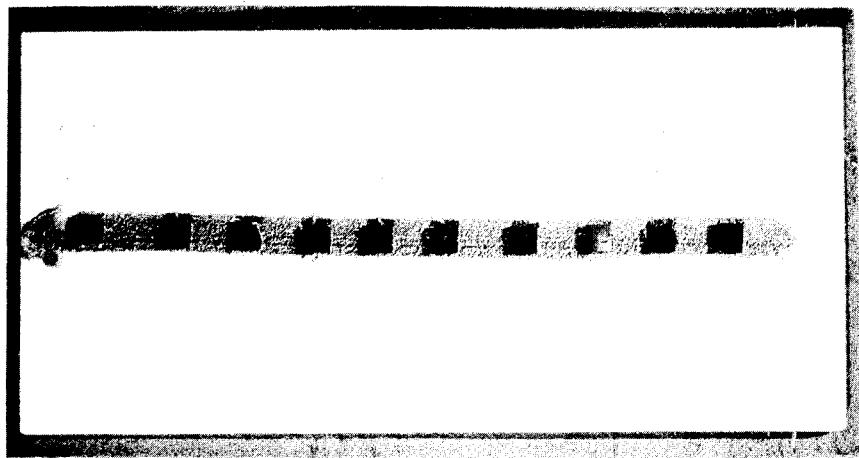
Figure 10. Typical bond strength specimen.
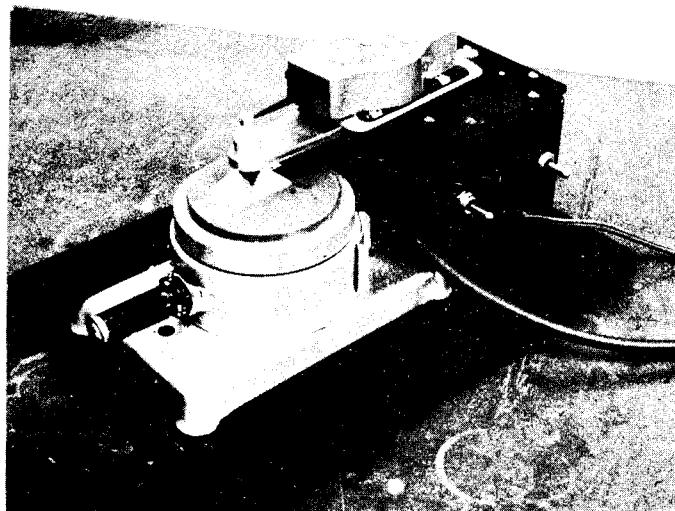
Figure 11. Bond strength tester.

Bond strengths were measured at both room temperature and at 150°C for freshly prepared specimens (i.e., immediately after cure) and at room temperature for specimens immersed for 30 min in isopropyl alcohol, Freon TF, and trichloroethylene, and for specimens aged for 10, 30, and 90 days at both room temperature and at 150°C.

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The electrically conductive adhesives tested and their cure schedules (recommended by the manufacturers) are as follows:

Adhesive	Cure Schedule
Ablebond 36-2 (silver filled)	30 min at 150°C
Epo-Tek H31 (silver filled)	1 hr at 150°C
Epo-Tek H21D (two-component silver filled)	10 min at 150°C
Ablebond 58-1 (gold filled)	30 min at 150°C
Epo-Tek H44 (gold filled)	1 hr at 150°C

Measurements also were made for the electrically insulative adhesive Ablefilm 517 (cured for 1 hr at 150°C).

Bond strengths at 150°C for the freshly prepared specimens are given in Table 1. In all other cases, the bond strengths exceeded the limit of the tester, 2.43×10^7 N/m^2 (3530 psi) except for the following:

Epo-Tek H31   After 10 days aging at room temperature
        9 exceeded the tester limit
        1 failed at 2.25×10^7 N/m^2 (3265 psi)

                      After 10 days aging at 150°C
        6 exceeded the tester limit
        4 averaged 2.01×10^7 N/m^2 (2910 psi)

                      After 30 days aging at 150°C
        9 exceeded the tester limit
        1 failed at 1.83×10^7 N/m^2 (2650 psi)

                      After 90 days aging at room temperature
        9 exceeded the tester limit
        1 failed at 2.25×10^7 N/m^2 (3265 psi)

Epo-Tek H21D   After 90 days aging at 150°C
        9 exceeded the tester limit
        1 failed at 2.31×10^7 N/m^2 (3350 psi)

In summary, these results show that:

1. The bond strengths of all adhesives are either unaffected or only slightly degraded by prolonged aging at room temperature or by prolonged exposure to the maximum-use temperature of 150°C.

TABLE 1. BOND STRENGTHS FOR FRESHLY PREPARED SPECIMENS

Adhesive	Measured at Room Temperature		Measured at 150°C	
	N/m²	psi	N/m²	psi
Ablefilm 517	$>2.43 \times 10^7$	>3530	8.21×10^6	1190
Ablebond 36-2	$>2.43 \times 10^7$	>3530	1.01×10^7	1465
Epo-Tek H31	$>2.43 \times 10^7$	>3530	1.61×10^7	2335
Epo-Tek H21D	$>2.43 \times 10^7$	>3530	5 > 2.43×10^7 5 av 2.10×10^7	5 > 3530 5 av 3050
Ablebond 58-1	$>2.43 \times 10^7$	>3530	9.31×10^6	1350
Epo-Tek H44	$>2.43 \times 10^7$	>3530	9 > 2.43×10^7 1 2.25×10^7	9 > 3530 1 3265

2.   The Epo-Tek adhesives have a much higher bond strength when measured at 150°C than the Ablestik adhesives. The gold-filled adhesive, Epo-Tek H44, essentially retains its room-temperature bond strength.

3.   The bond strengths of all adhesives were unaffected by prolonged immersion in commonly used cleaning solvents.

Outgassing After Cure

Long-term outgassing data after cure were obtained for the following electrically conductive adhesives:

Adhesive	Cure Schedule
Ablebond 36-2 (silver filled)	30 min at 150°C
Epo-Tek H31 (silver filled)	1 hr at 150°C
Epo-Tek H21D (two-component silver filled)	10 min at 150°C
DuPont 5504 (silver filled)	1 hr at 150°C
Ablebond 606-1 (silver filled)	30 min at 150°C
Ablebond 58-1 (gold filled)	30 min at 150°C
Epo-Tek H44 (gold filled)	1 hr at 150°C

Also, tests were run for two samples of the electrically insulative adhesive Ablefilm 517. One was cured normally (i.e., 1 hr at 150°C); the other was cured for 1 hr at 150°C and then vacuum-baked for 2 hr at 150°C and 10 to 100 μm of Hg to see if this treatment would reduce the observed high outgassing. The cure schedules used for all adhesives were specifically recommended as optimum by their manufacturers.

Testing was performed by a method previously used for evaluating the electrically insulative adhesives. Precisely weighed 1-gm samples of cured adhesive were sealed in breakseal tubes equipped with manometers. The break-seal tubes were evacuated, sealed, mounted on a rack, and placed in a 150°C oven. Pressure versus time readings were then taken over an extended period. The results are shown in Figures 12 through 20.

An analysis of the curves for the silver-filled adhesives shows that Ablebond 36-2 was the lowest outgasser, Depont 5504 was the second lowest, and Ablebond 606-1 was by far the largest. Also, both of the Epo-Tek adhesives (H21D and H31) were substantial outgassers. However, after its initial surge of outgassing, Epo-Tek H21D outgassed very little, if any, during continued aging, indicating that this adhesive is chemically stable at 150°C. On the contrary, the data for Epo-Tek H31 indicate that several rather pronounced changes in its outgassing rate occurred during extended aging. These changes
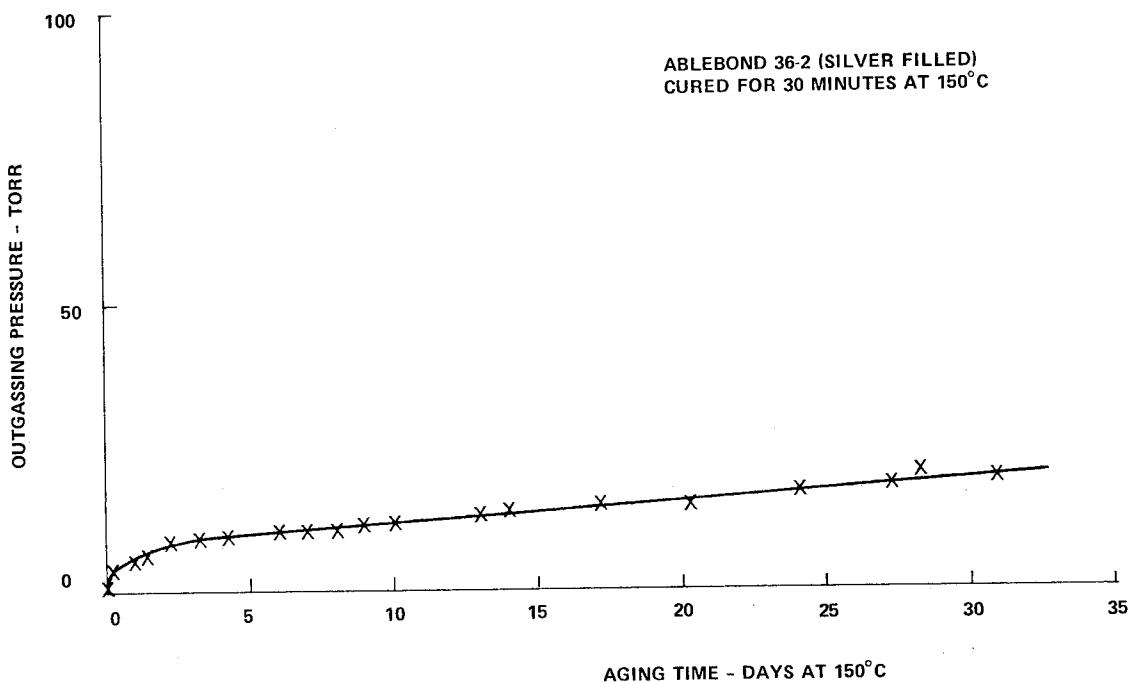

Figure 12. Outgassing (at 150°C) of Ablebond 36-2 after cure.
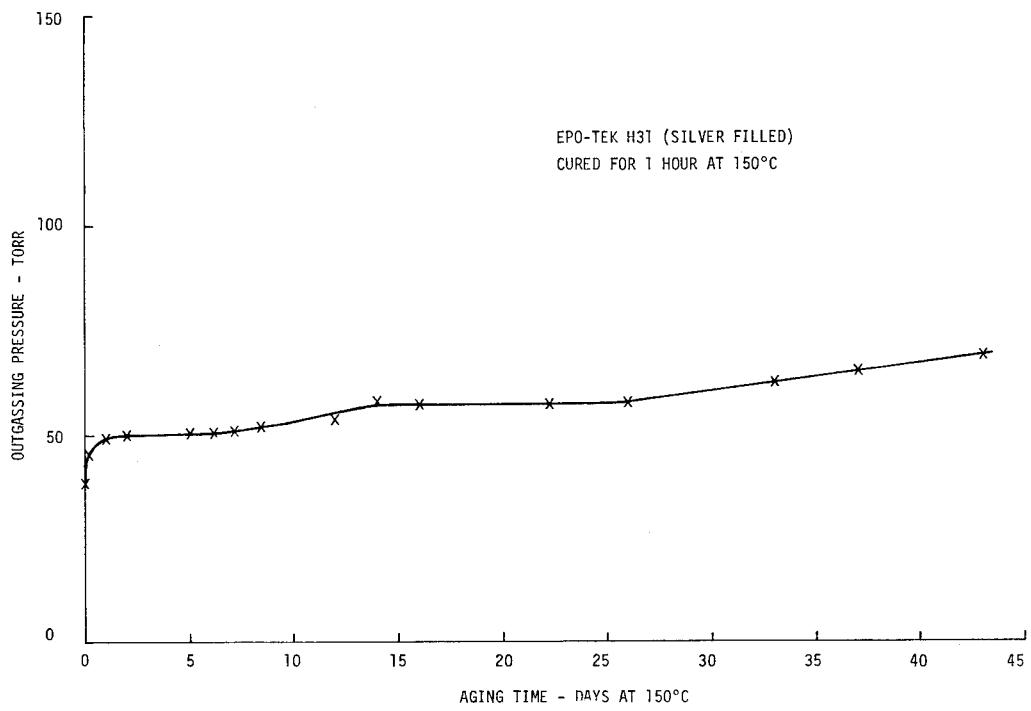
Figure 13. Outgassing (at 150°C) of Epo-Tek H31 after cure.
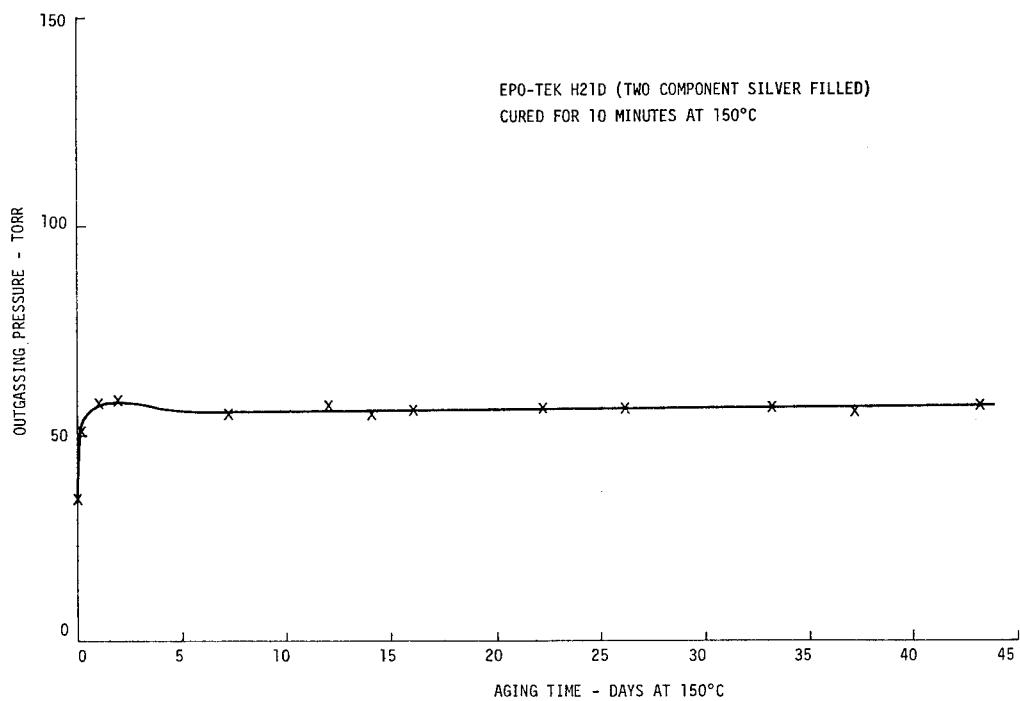
Figure 14. Outgassing (at 150°C) of Epo-Tek H21D after cure.
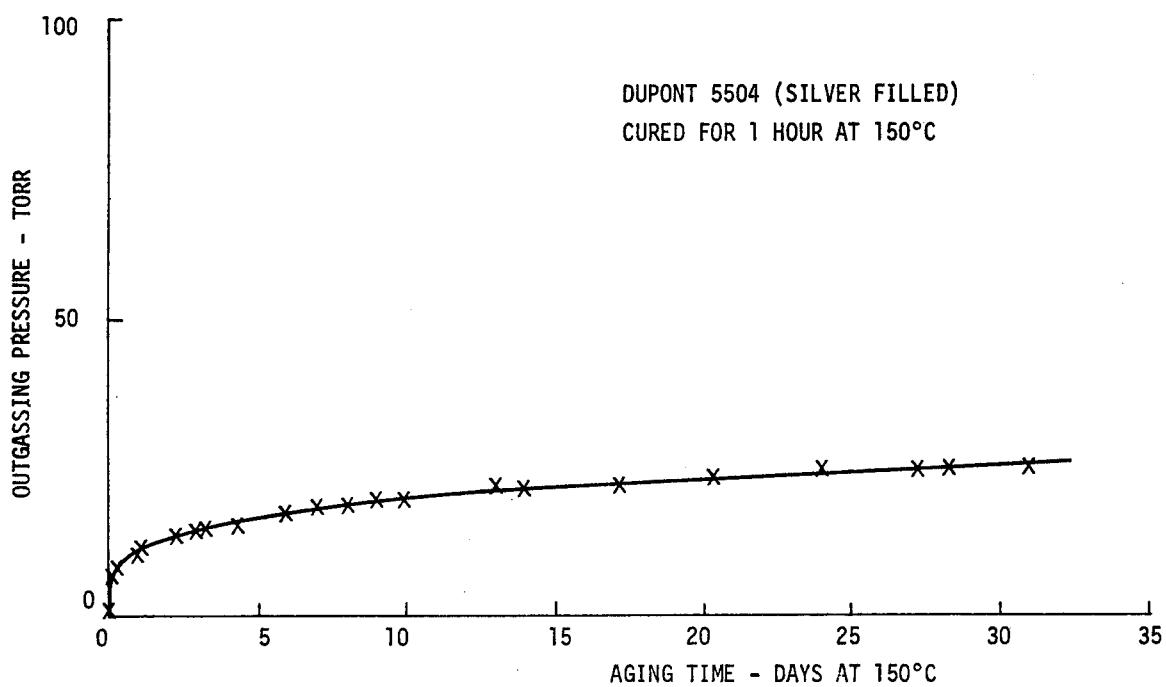
Figure 15. Outgassing (at 150°C) of DuPont 5504 after cure.
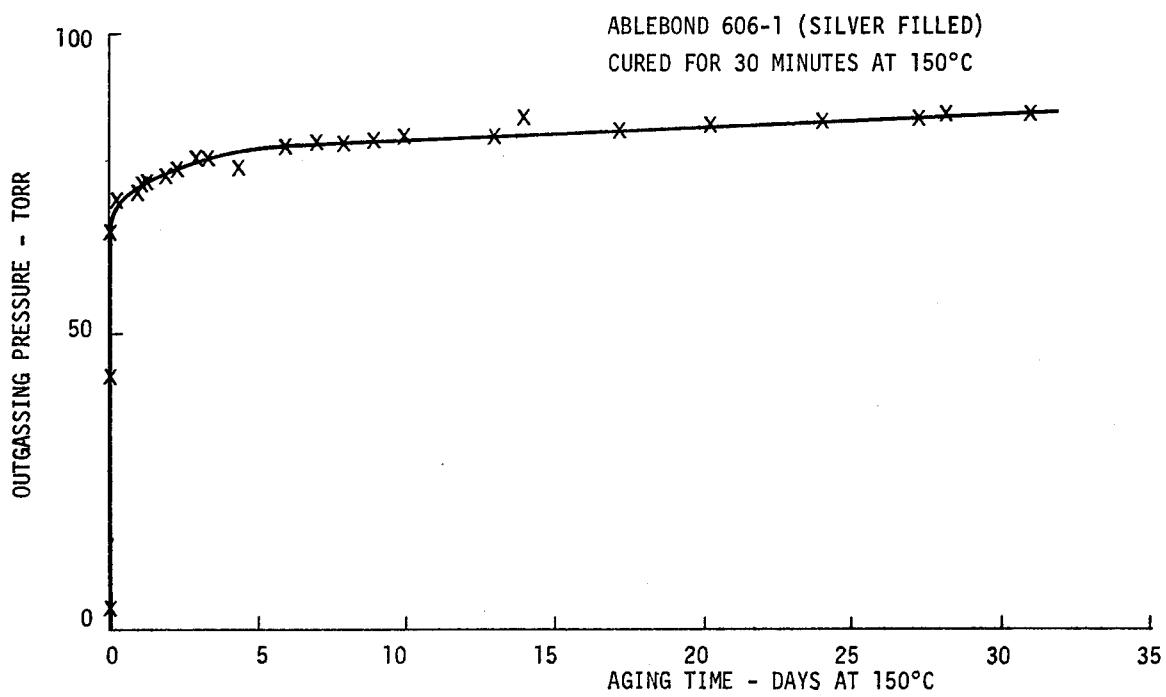
Figure 16. Outgassing (at 150°C) of Ablebond 606-1 after cure.

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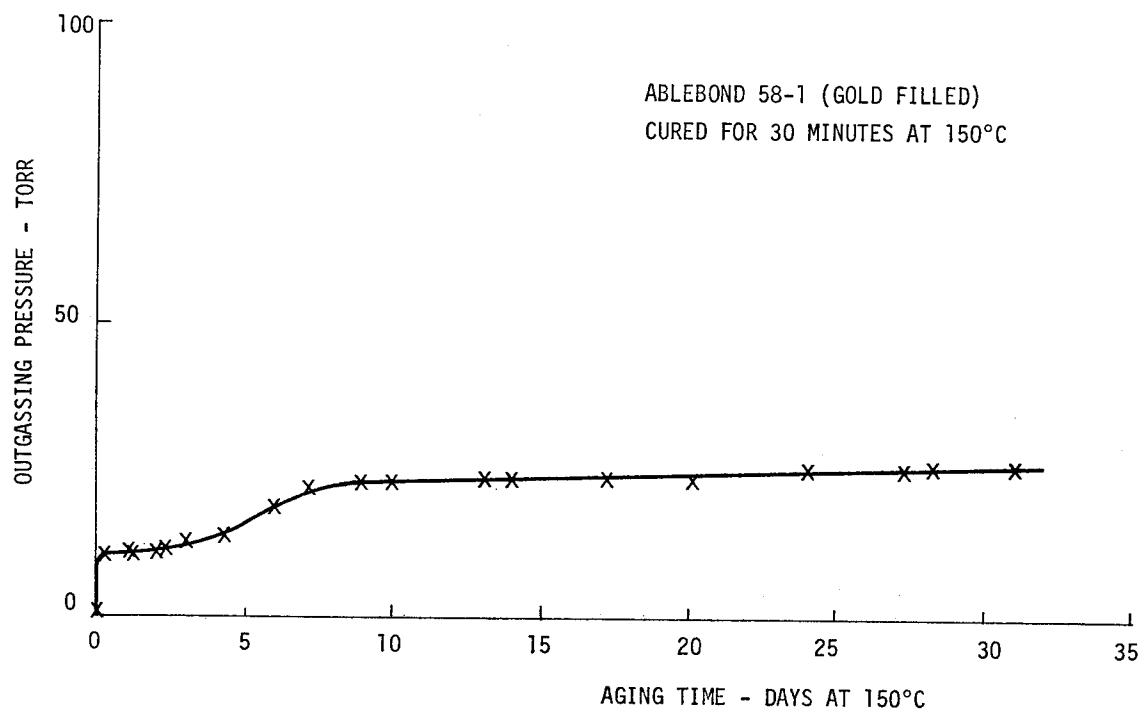
Figure 17. Outgassing (at 150°C) of Ablebond 58-1 after cure.
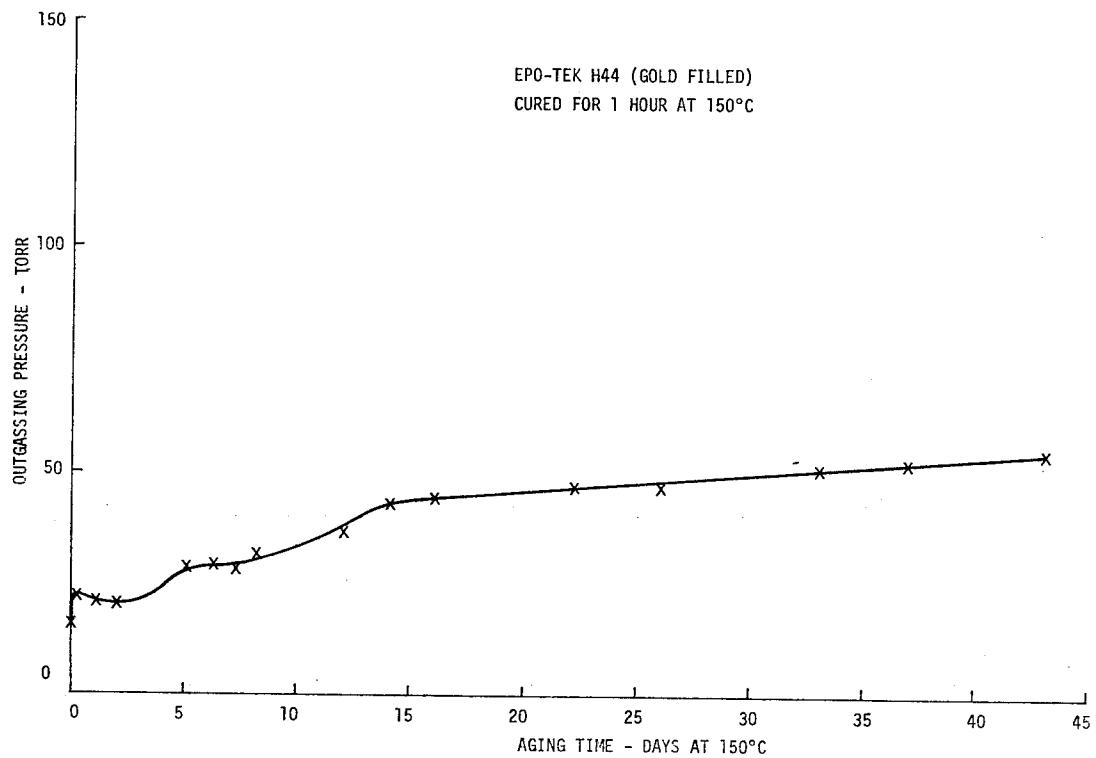
Figure 18. Outgassing (at 150°C) of Epo-Tek H44 after cure.
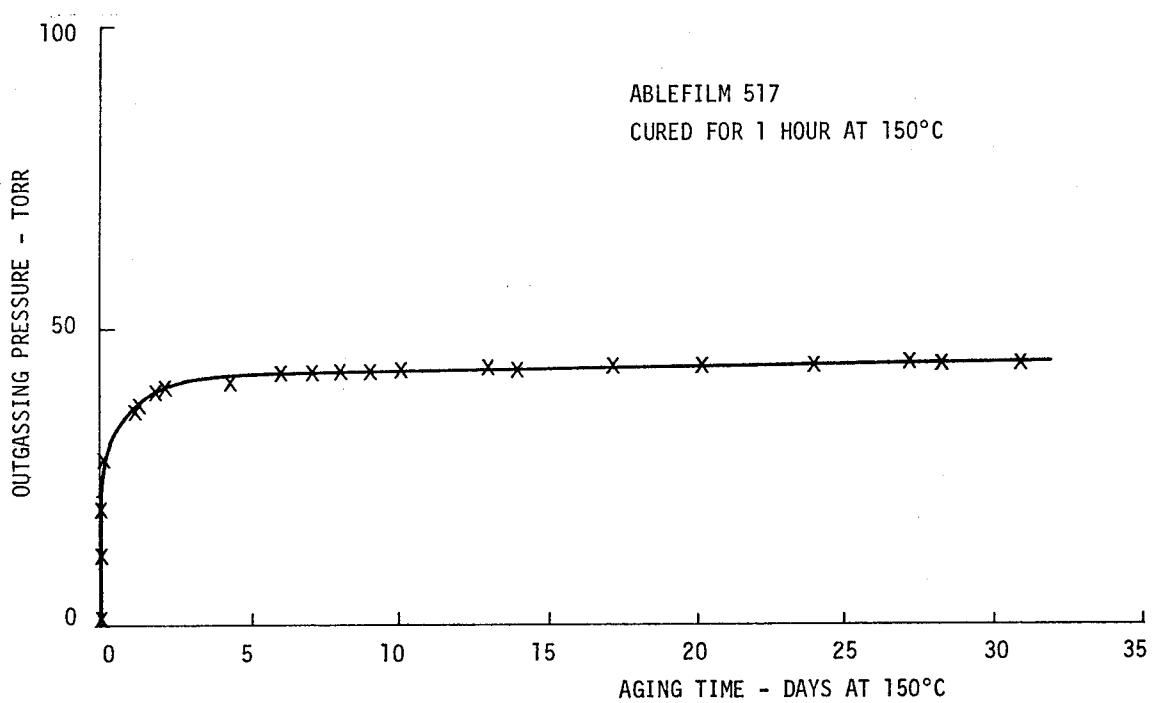
Figure 19. Outgassing (at 150°C) of Ablefilm 517 after normal cure.
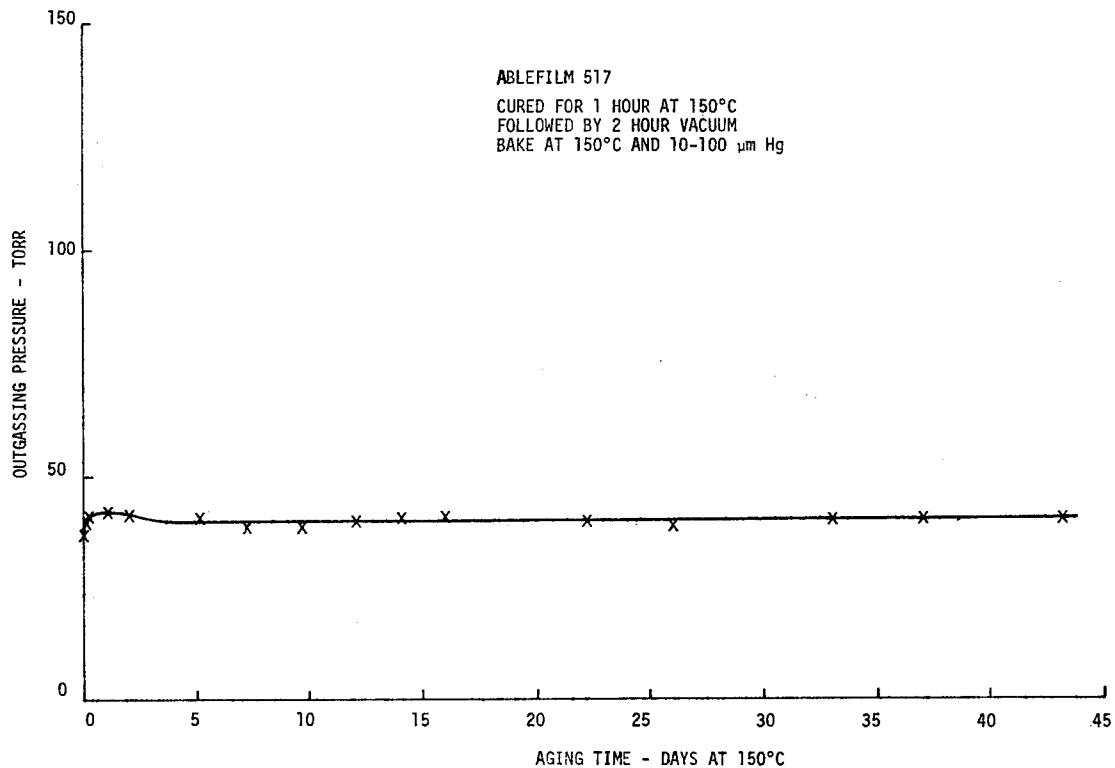

Figure 20. Outgassing (at 150°C) of Ablefilm 517 after normal cure
followed by vacuum bake.

are assumed to be due to changes in the chemical structure of the adhesive. The sudden increase from essentially zero outgassing to a rather large out-gassing rate at 25 to 26 days may indicate that this adhesive is decomposing.

Comparison of the curves for the gold-filled adhesives shows that Able-bond 58-1 is a substantially lower outgasser than Epo-Tek H44 and is comparable to the silver-filled adhesive DuPont 5504. Also, the behavior of Epo-Tek H44 is similar to that for the silver-filled adhesive Epo-Tek H31, and it was still outgassing at a substantial rate at the end of 40 days. As in the case of Epo-Tek H31, this may be indicative of decomposition.

Comparison of the curves obtained for Ablefilm 517 shows that the pressure due to outgassing is essentially the same in both cases. Certainly, the results agree within the accuracy limits of the experiment. Thus, apparently nothing (or at least very little) is gained by additional processing of the adhesive after its normal cure of 1 hr at 150°C.

Corrosivity

Electrically Insulative Adhesives. The same five electrically insulative adhesives previously evaluated and reported on in NASA TM X-64789 (except that Ablefilm 517 was used instead of Ablefilm 517A) were again tested. These adhesives were Hysol 0151, Ablefilm 517, Eccobond 104, Epo-Tek H74, and Epo-Tek H61. Specimens were prepared as before, and corrosivity was deter-mined for thin-film aluminum and both thin- and thick-film gold. Previously, corrosivity was determined for a 24-hr exposure to an 85°C/100-percent relative humidity environment with 50 V applied to line pairs 1, 3, 5 and 7 with line pairs 2, 4 and 6 left open. In the present evaluation specimens were exposed for 24 hr to an 80 to 85°C/80- to 85-percent relative humidity environ-ment (or more precisely, 82°C/84-percent RH) with 30 V applied to line pairs 1, 3, 5 and 7 with line pairs 2, 4 and 6 left open.

Test specimens (Fig. 21) consisted of seven pairs of parallel lines on a 1.90- by 3.81-cm (0.75- by 1.50-in.) unglazed alumina substrate. The line dimensions were as follows:

1. Thin-Film Corrosion Pattern

    2 pairs — 0.0127-cm (5 mils) wide, 0.00635-cm (2.5 mils) spacing

    2 pairs — 0.0254-cm (10 mils) wide, 0.0127-cm (5 mils) spacing

    2 pairs — 0.0254-cm (10 mils) wide, 0.0254-cm (10 mils) spacing

    1 pair — 0.0254-cm (10 mils) wide, 0.0508-cm (20 mils) spacing
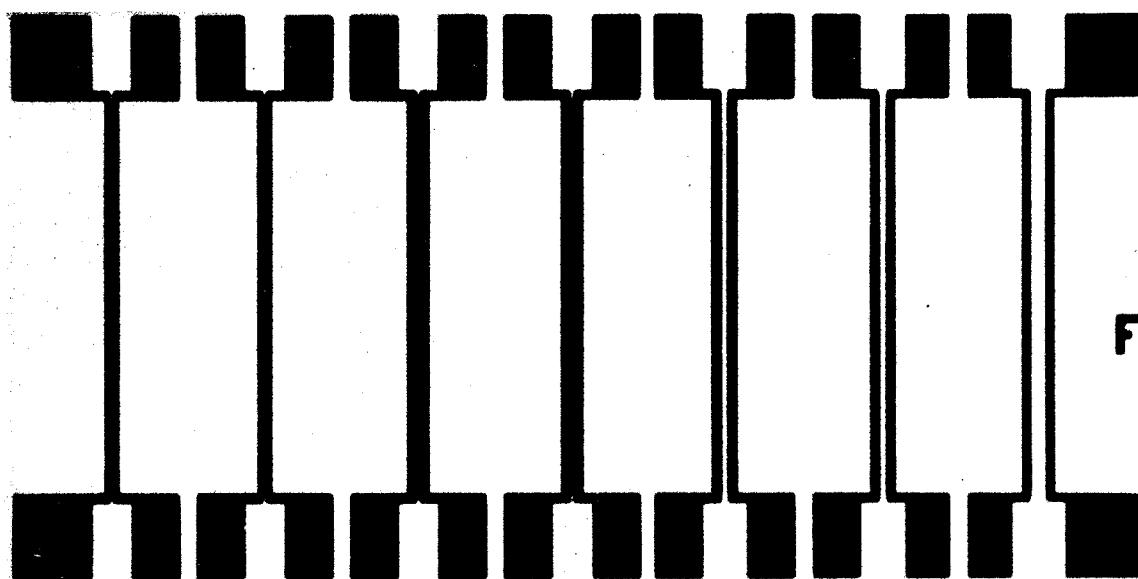
Figure 21. Corrosivity test specimen (line pairs are counted
1 through 7 from left to right).

2.   Thick-Film Corrosion Pattern

This pattern is the same as the thin-film pattern except that the spacing
of the first two pairs of lines is 0.0127 cm (5 mils) because of the limitation of
screened and fired thick-film processing.

Metallization systems used were as follows:

1.   Thin-Film Aluminum

Nichrome $\approx$ 10 nm (100 Å) (to improve adhesion)

Aluminum $\approx$ 1000 nm (10 000 Å)

2.   Thin-Film Gold

Nichrome $\approx$ 17 nm (170 Å) (to improve adhesion)

Nickel $\approx$ 100 nm (1000 Å) (chromium diffusion barrier)

Vacuum-Deposited Gold $\approx$ 1000 nm (10 000 Å)

Electro-Plated Gold $\approx$ 2500 nm (25 000 Å)

3. Thick-Film Gold

   Conductor Ink — EMCA 212B

   Thickness — 0.00178 cm (0.7 mil)

   Firing Temperature — 990 +10, -5°C

Test specimens were prepared by placing dots of adhesive across each line pair and curing according to the manufacturers' recommendations as follows:

Adhesive	Cure Schedule
Hysol 0151	2 hr at 60°C
Ablefilm 517	30 min at 150°C
Eccobond 104	3 hr at 150°C
Epo-Tek H74	40 min at 100°C
Epo-Tek H61	1 hr at 150°C

Evaluation was made by (1) visual examination at 30X, (2) measurement of the resistance of each of the individual lines, and (3) measurement of the interline or insulation resistance of each of the line pairs before and after exposure to the test conditions. Photographs taken of the specimens at the end of the tests are presented in Figures 22 through 36. A discussion of the test results follows. As noted, in some cases line pairs arced over during application of the high voltage required to measure the interline or insulation resistance. Evidence of such arcing is obvious and is easily distinguished from corrosion.

1. Hysol 0151

   a. Thin-Film Aluminum — No visual evidence of corrosion.

   b. Thin-Film Gold — Discoloration under adhesive of all positive lines, ranging from light red or pink on inner edge and extending across a rather large portion of the line width for line pair 1 to only slight discoloration of inner edge for line pair 7. Three arcing spots on line pair 3 (two of which are under the adhesive) and two spots on line pair 5. Arcing under adhesive on line pair 3 occurred while interline resistance was being measured.
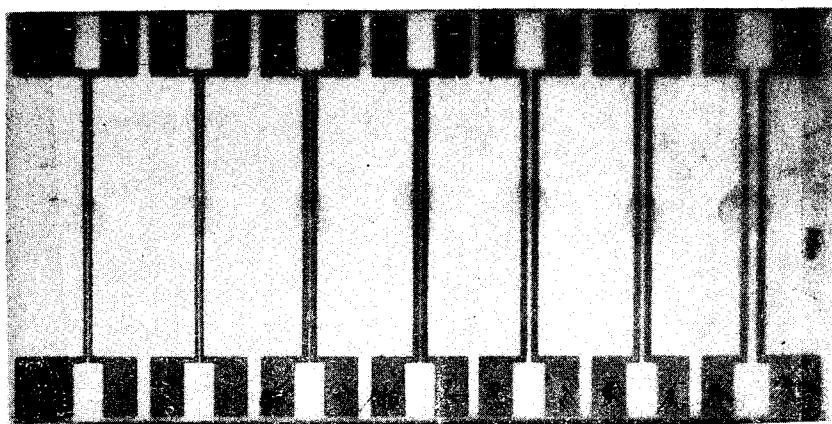
Figure 22. Hysol 0151, thin-film aluminum.
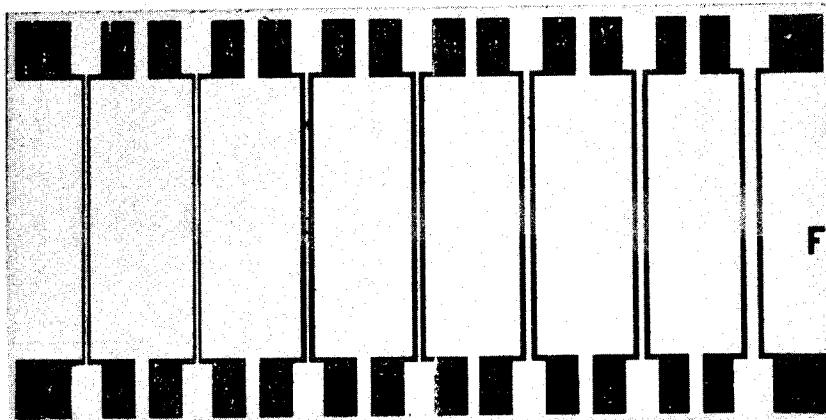
Figure 23. Hysol 0151, thin-film gold.
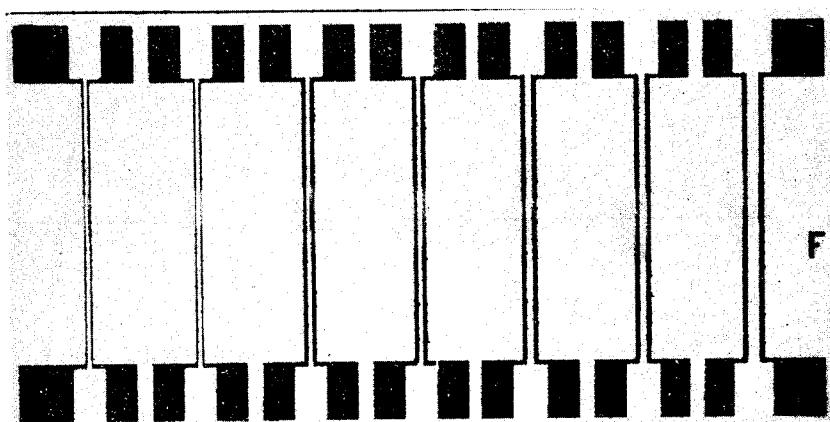
Figure 24. Hysol 0151, thick-film gold.
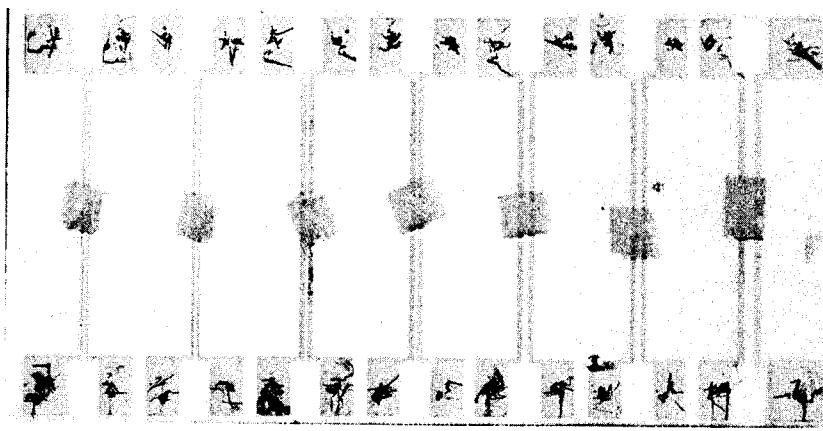
Figure 25. Ablefilm 517, thin-film aluminum.
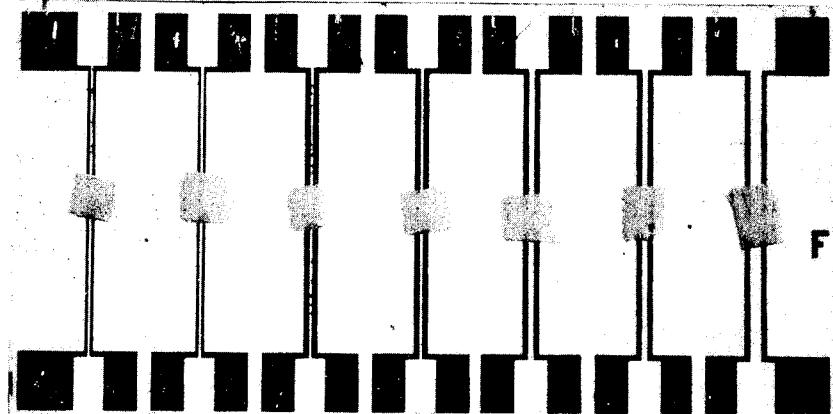
Figure 26. Ablefilm 517, thin-film gold.
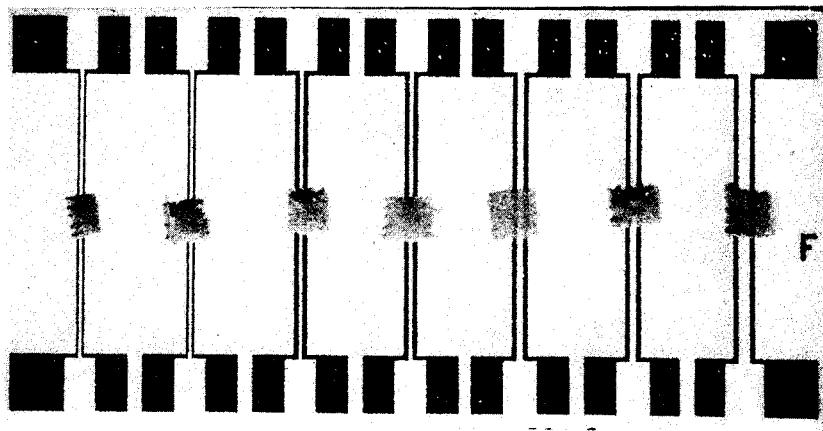
Figure 27. Ablefilm 517, thick-film gold.
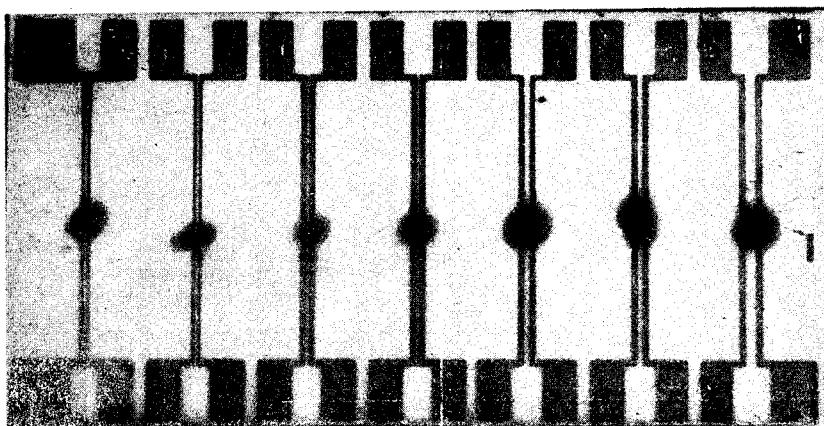
Figure 28. Eccobond 104, thin-film aluminum.
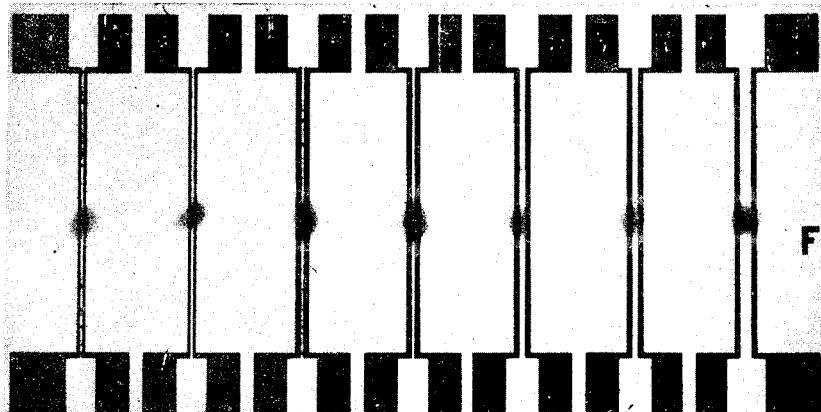
Figure 29. Eccobond 104, thin-film gold.
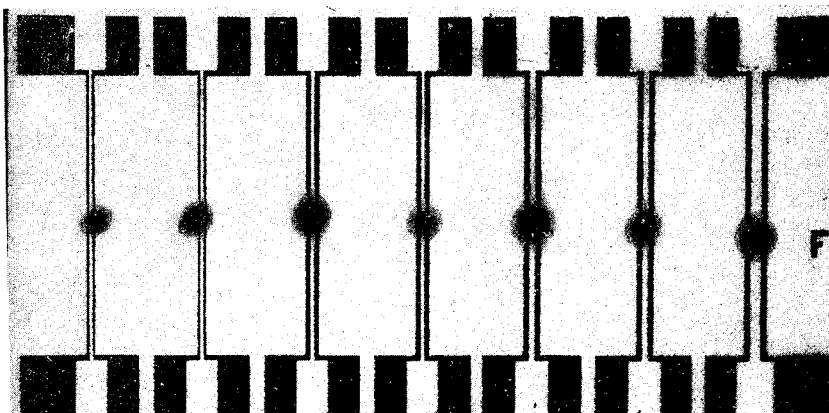
Figure 30. Eccobond 104, thick-film gold.
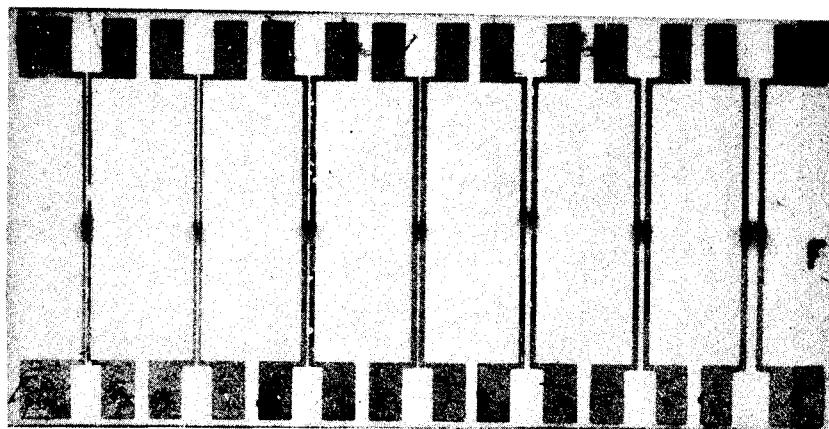
Figure 31. Epo-Tek H74, thin-film aluminum.
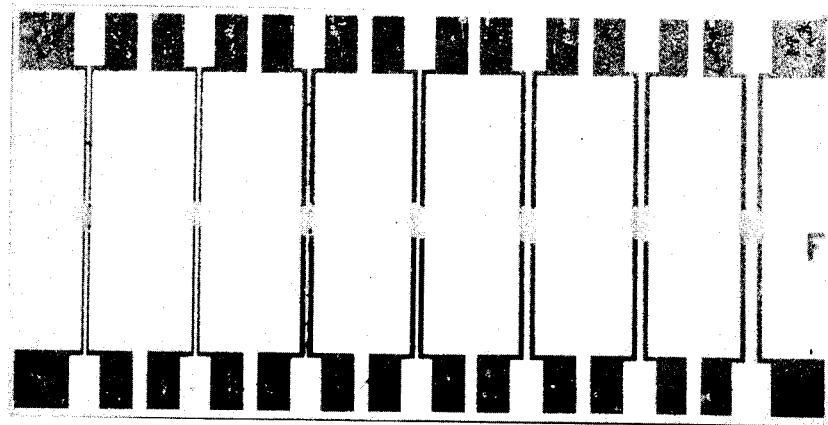
Figure 32. Epo-Tek H74, thin-film gold.
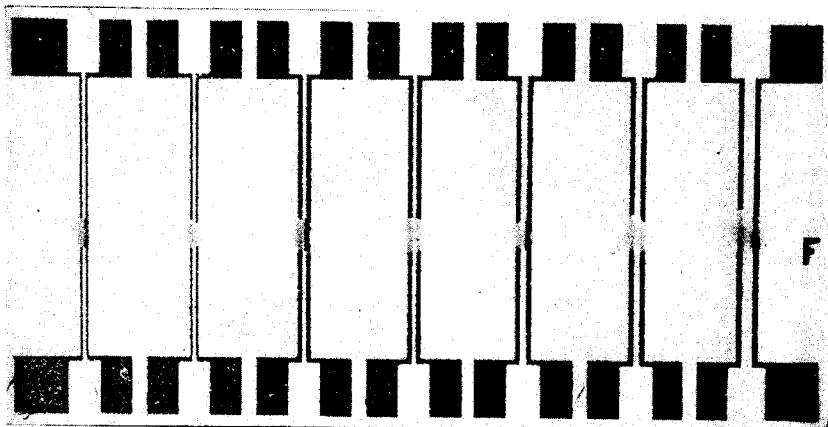
Figure 33. Epo-Tek H74, thick-film gold.
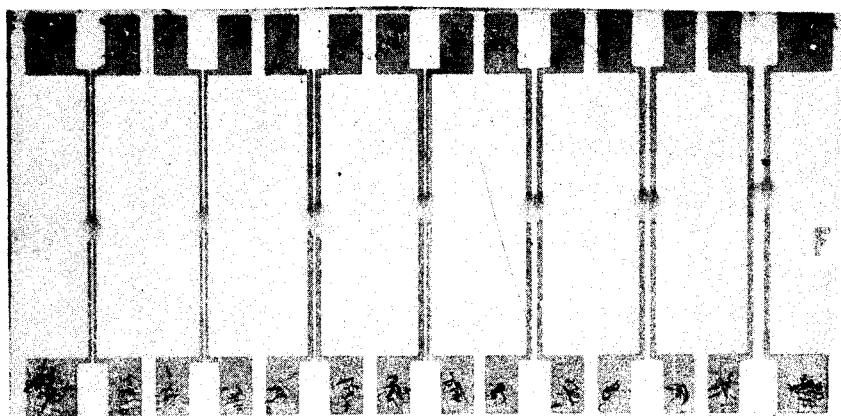
Figure 34. Epo-Tek H61, thin-film aluminum.
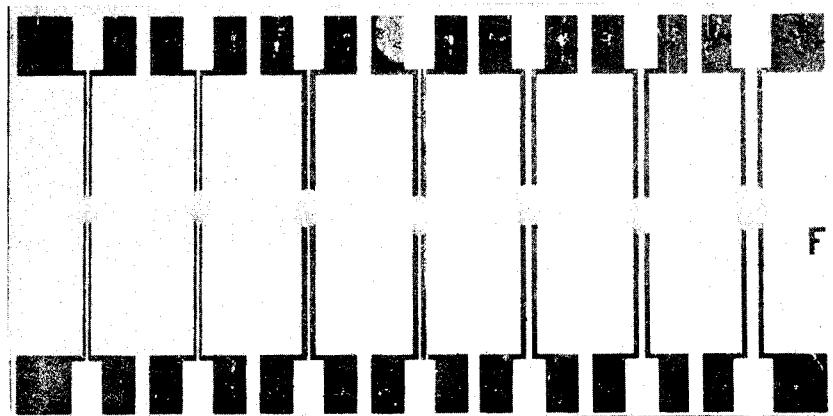
Figure 35. Epo-Tek H61, thin-film gold.
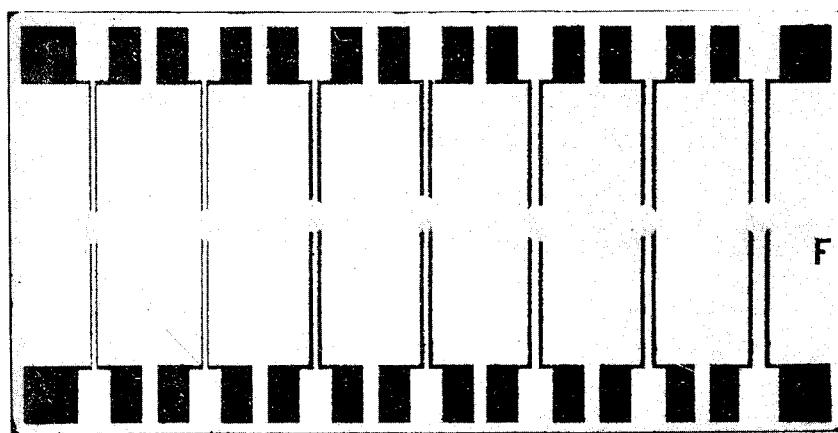
Figure 36. Epo-Tek H61, thick-film gold.

c. Thick-Film Gold — Very dark red or black discoloration of inner edge of all positive lines with lighter pinkish-red discoloration extending further across lines in some cases.

2. Ablefilm 517

a. Thin-Film Aluminum — No visual evidence of corrosion due to adhesive. Slight buildup of white material (probably Al_2O_3) remote from adhesive on positive line of line pair 3. Measurement shows that the resistance of this line has increased slightly.

b. Thin-Film Gold — No visual evidence of corrosion. However, arcing has occurred on line pairs 1 and 3.

c. Thick-Film Gold — No visual evidence of corrosion.

3. Eccobond 104

a. Thin-Film Aluminum — No visual evidence of corrosion due to adhesive. However, one darkened spot on line pair 1 and two on line pair 3 remote from adhesive.

b. Thin-Film Gold — No visual evidence of corrosion. However, considerable arcing has occurred on line pairs 1 and 3, and slight arcing has occurred on line pairs 5 and 7.

c. Thick-Film Gold — No visual evidence of corrosion.

4. Epo-Tek H74

a. Thin-Film Aluminum — Corrosion of positive lines of all line pairs. Lines are darkened at and extending from adhesive. Extent of darkened portion of line decreases as line spacing increases. Resistance measurements show that all positive lines are open (i.e., greater than 50 Ω).

b. Thin-Film Gold — Discoloration of all positive lines under adhesive; complete and deep purple or black for line pair 1, progressively lessening to partial and purplish brown for line pair 3, and slight and light brown for line pairs 5 and 7. Also, one arced spot on line pair 1, and several on line pair 3.

c. Thick-Film Gold — Dark purple to black discoloration under adhesive of all positive lines. Measurements indicate a decrease in interline resistance of about an order of magnitude.

5. Epo-Tek H61

a. Thin-Film Aluminum — No visual evidence of corrosion due to adhesive. One corroded spot, remote from adhesive, at top of right line of line pair 4.

b. Thin-Film Gold — No visual evidence of corrosion.

c. Thick-Film Gold — Small dark dots at adhesive-gold interfaces at edges of all positive lines (adhesive-gold-ceramic interface points).

In all cases, except for the spot (remote from the adhesive at the top of the right line of line pair 4) mentioned for the Epo-Tek H61 thin-film aluminum specimen, all line pairs which did not have voltage applied to them showed no evidence of corrosion. Also, except where stated, measurements did not indicate changes in line or interline resistance of any significance.

The preceding results support the following general conclusions:

1. In all cases when corrosion or discoloration occurred, it occurred on the positive lines of the line pairs. This confirms the results reported previously in NASA TM X-64789 in which more severe test conditions were used (85°C/100-percent relative humidity with 50 V applied to line pairs).

2. There was no evidence of corrosion for any of the three metallization systems by Ablefilm 517 (tertiary amine cured) or Eccobond 104 (anhydride cured). The only evidence of any effect by Epo-Tek H61 (boron trifluoride complex-cured) was the formation of very small dark dots at the adhesive-gold-ceramic interface points on the thick-film gold metallization system. Hysol 0151 (primary, secondary amine cured) did not affect thin-film aluminum metallization but caused some discoloration of both thin- and thick-film gold metallizations. Epo-Tek H74 (probably imidazole cured) severely corroded the thin-film aluminum metallization and caused discoloration of both thin- and thick-film gold metallizations.

3. The adhesives ranked in order of increasing corrosivity are:

(a) Eccobond 104 or Ablefilm 517

(b) Epo-Tek H61

(c) Hysol 0151

(d) Epo-Tek H74

This conclusion differs from that previously given in NASA TM X-64789 only in the interchange of Hysol 0151 and Epo-Tek H61.

Electrically Conductive Adhesives. Initially, testing to determine the corrosivity of selected electrically conductive adhesives was made by preparing specimens consisting of the different metallization systems with dots of the adhesives on them and visually observing these specimens for evidence of corrosion as a function of time. Thin-film aluminum and thin-film gold metallization specimens prepared on glass slides and thick-film gold metallization specimens prepared on alumina substrates were used. Five adhesives were evaluated: Ablebond 36-2 and Epo-Tek H31 (single component silver filled), Epo-Tek H21D (two component silver filled), and Ablebond 58-1 and Epo-Tek H44 (single component gold filled).

Both cured and uncured specimens were tested. Uncured specimens were aged at room conditions, and cured specimens were aged at both room conditions and at 150°C. Results obtained from visual observations at the end of 24, 200 and 1200 hr are given in Table 2.

A summary of these results is as follows:

1.   The silver-filled adhesives Ablebond 36-2 and Epo-Tek H21D and the gold-filled adhesive Ablebond 58-1 did not corrode any of the metallizations under any conditions. In the case of Epo-Tek H21D, the uncured specimens had hardened and it was impossible to remove dots for direct observation, but other evidence supports this conclusion.

2.   The silver-filled adhesive Epo-Tek H31 did not corrode the thick-film gold metallization but did corrode the thin-film aluminum metallization and possibly caused minor corrosion of the thin-film gold metallization.

3.   The gold-filled adhesive Epo-Tek H31 did not corrode the thin- or thick-film gold metallizations but did corrode the thin-film aluminum metallization.

While this test is simple to perform and gave useful comparative data, it is considered too qualitative and subjective to serve as a practical evaluation method. Consequently, to get more quantitative data concerning the corrosivity

TABLE 2. CORROSIVITY OF ELECTRICALLY CONDUCTIVE ADHESIVES

Adhesive	After 24 hr	After 200 hr	After 1200 hr
Ablebond 36-2	No effect on any metallization under any condition.	Uncured specimens are still soft. No effect an any metallization under any condition. However, for specimens aged at 150°C, adhesive has discolored as follows: Thin-Film Aluminum — rather broad reddish-gold band on edge of adhesive. Thin- and Thick-Film Gold — narrow gold-colored band on edge of adhesive.	Uncured specimens are still soft. For specimens aged at 150°C, adhesive has turned a dark bluish-gray. Also, there is a rather extensive orange-red discoloration around the adhesive on both thin- and thick-film gold specimens. Removal of two dots of adhesive from uncured specimens (using acetone and alcohol) showed no evidence of any interaction with any of the metallizations.
Epo-Tek H31	Effect only on thin-film aluminum as follows: Uncured — broad, dull white halo (not shiny like epoxy). Cured (aged at RT) — halo as above but not nearly as broad. Cured (aged at 150°C) — halo as for cured (aged at RT) but darker. The inside is purple-black.	Uncured specimens are still soft. Effect only on thin-film aluminum as follows: Uncured — halo as before but separated from adhesive. Cured (aged at RT and 150°C) — halo as before.	Uncured specimens are still soft. For all specimens except those aged at 150°C, the major effect is on the thin-film aluminum metallization and is essentially as before. For thick-film gold specimens aged at 150°C, appearance is similar to that for Ablebond 36-2. For thin-film gold specimens aged at 150°C, broad blue ring and a reddish-brown outer ring developed around the adhesive. Removal of two dots of adhesive from uncured specimens showed no evidence of adhesive having interacted with the thick-film gold specimen, a very slight stain on the thin gold specimen and a very definite spot on the thin-film aluminum specimen. Also, the halo on the thin-film aluminum specimen remains unchanged (i.e., is not removed by solvents).
Epo-Tek H21D	Effect only on thin-film gold as follows: Uncured — broad, dull halo (makes gold more yellow). Probably due to runout or bleeding of epoxy.	Uncured specimens are hard. Effect only on thin-film gold same as before.	Effect only on thin-film gold as before. Since uncured adhesive is hard, dots could not be removed to check for evidence of corrosion.

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TABLE 2. (Concluded)

Adhesive	After 24 hr	After 200 hr	After 1200 hr
Epo-Tek H21D (Concluded)	Cured (aged at RT) — halo as before but gold is a little more golden. Cured (aged at 150°C) — as for uncured.		
Ablebond 58-1	No effect on any metallization under any condition.	Uncured specimens are still soft. No effect on any metallization under any condition.	Uncured specimens are still soft. No evidence of corrosion on any metallization under any condition. For uncured specimens there is evidence of slight runout or separation of epoxy on thin-film aluminum metallization and considerable runout on thin-film gold metallization. Removal of two dots of adhesive from uncured specimens showed no evidence of any interaction with either the thin-film gold or aluminum metallization and only a very slight stain on the thick-film gold metallization.
Epo-Tek H44	Effect only on thin-film aluminum as follows: Uncured — broad, dull white halo (not shiny like epoxy) Cured (aged at RT and 150°C) — halo as above but not as broad.	Uncured specimens are still soft. Effect only on thin film aluminum as follows: Uncured — broad, dull white halo as before. However, in several cases the halo is separated from the adhesive, and in some cases this separation area is spectral. Cured (aged at RT and 150°C) — as before.	Uncured specimens are still soft. Effect only on thin-film aluminum metallization as before. On specimens aged at 150°C, the adhesive is much darker (deep brownish-red) and has a burnt appearance compared with specimens aged at room temperature. Also, the adhesive has a much glossier appearance and there is some evidence of runout or separation of epoxy. Removal of two dots of adhesive from uncured specimens showed no evidence of interaction except on thin-film aluminum metallization. In this case there is a very definite spot which has a spectral appearance. Also, the halo remains unchanged (i.e., is not removed by solvents).

of the electrically conductive adhesives, tests were devised and performed using the same test pattern previously used to evaluate the corrosivity of the electrically insulative adhesives. Of course, because these adhesives are electrically conductive rather than insulative, the testing method had to be modified.

For this evaluation, two specimens of each metallization (thin-film aluminum and thin- and thick-film gold) were prepared for each adhesive. On one set of specimens, a dot of adhesive was applied to each line. Dots on the lines of the same line pair were offset from each other by at least 0.5 cm. On the other set of specimens, a dot of adhesive was applied so as to bridge the lines of each line pair. Photographs of typical specimens are given in Figure 37. Test specimens were exposed to an 80-85°C/80-85 -percent relative humidity environment for 24 hr with 30 V applied between the lines of alternate line pairs (line pairs 1, 3, 5, and 7) for the specimens with dots of adhesive on each line and with approximately 20 mA of current flowing through the lines of alternate line pairs (line pairs 1, 3, 5, and 7) for the specimens with adhesive bridging the lines. Corrosion effects were determined by visual examination at 30X and by comparison of line and interline resistances measured before and after exposure to the test environment. Adhesives tested and their cure schedules (recommended by the adhesive manufacturers) were as follows:

1. Silver Filled

    a. Ablebond 36-2 — 30 min at 150°C

    b. Epo-Tek H31 — 1 hr at 150°C

2. Gold Filled

    a. Ablebond 58-1 — 30 min at 150°C

    b. Epo-Tek H44 — 1 hr at 150°C

A discussion of the results obtained from this investigation follows. The only specimens that showed any visual evidence of corrosion were the thin-film aluminum specimens with dots of Ablebond 58-1 and Epo-Tek H44 bridging the line pairs. For these specimens, all lines were darkened around the adhesive dots in the halo area to a distance of about 1/2- to 1-dot radius for Epo-Tek H44 and to a distance of about 1-dot radius for Ablebond 58-1. Photographs of these specimens are given in Figures 38 and 39. Photographs of the other test specimens are not included since there was no visual evidence of corrosion.
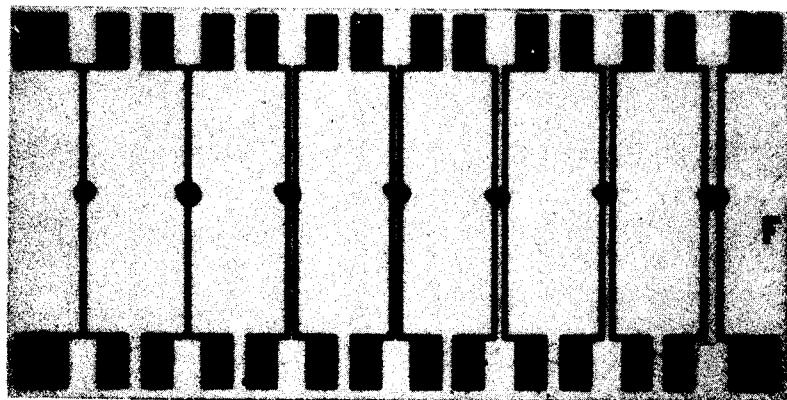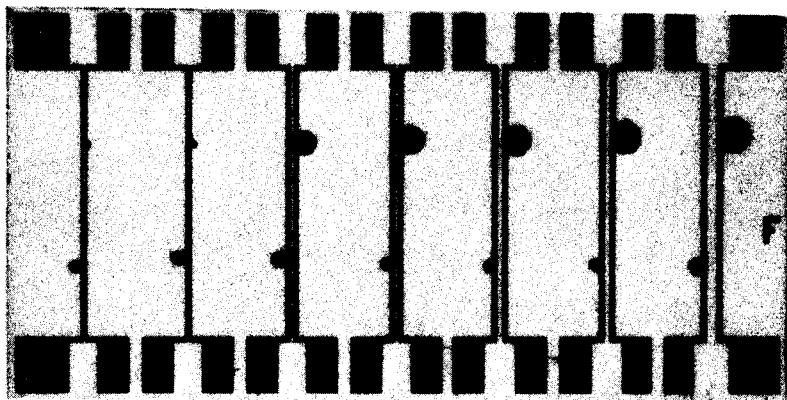
Figure 37. Typical corrosivity test specimens for electrically conductive adhesives.
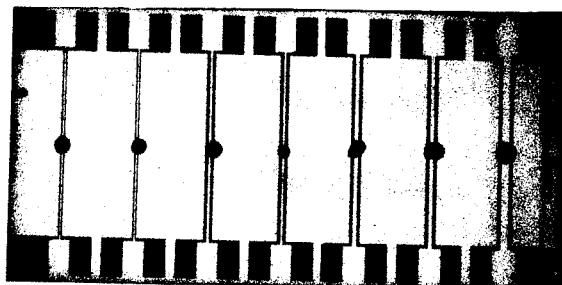

Figure 38. Epo-Tek H44, thin-film aluminum adhesive dots bridging lines.
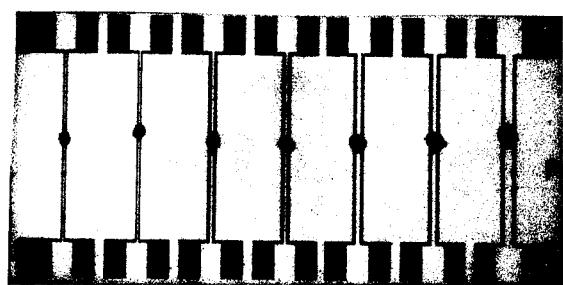
Figure 39. Ablebond 58-1, thin-film aluminum adhesive dots bridging lines.

Resistance data for the specimens with adhesive dots bridging the lines of each line pair indicated no corrosion for any of the specimens except the thin-film aluminum specimen with Ablebond 36-2. For this specimen, the resistances of all lines, even those that did not have current flowing through them during test, increased substantially from a few ohms before exposure to greater than 50 Ω after exposure. Fifty Ω is the maximum reading obtainable on the Simpson Model 1699 Multi-Range Precision Milliohmmeter used to measure line resistance. For the purposes of the present test, 50 Ω is considered to be an open circuit.

Some specimens with dots of adhesive bridging the lines showed surprising changes in interline resistance. For Ablebond 36-2, the interline resistances of the thin-film aluminum specimen were found to be greater than 50 Ω immediately after cure when measured using the Simpson Model 1699 Milliohmmeter. These resistances were greater than 1000 Ω on the 1 kΩ scale of the Triplet VOM but switched to less than 50 Ω when the output of the 100 kΩ scale of the Triplet VOM (18 V) was applied to them. However, after exposure to the test environment they again were found to be greater than 50 Ω. A similar situation occurred for the thin-film aluminum specimens for Epo-Tek H31 and Epo-Tek H44. Also, the interline resistance for Ablebond 36-2 on thin-film gold and for Ablebond 58-1 on thin-film aluminum was found to have increased to greater than 50 Ω after exposure to the test environment.

A different situation occurred for Epo-Tek H31 on the thin- and thick-film gold metallizations. For the thin-film gold specimen, the interline resistances of all line pairs through which current was passed during the test decreased in value, while the interline resistances of those line pairs which did not have current flowing through them did not change. For the thick-film gold specimen, the interline resistances of all line pairs decreased in value after exposure to the test environment — even those line pairs which did not have current flowing through them during test.

An explanation of this phenomenon cannot be made at this time, but a thorough investigation of it and its bearing on circuit reliability should be made.

Weight Loss

Thermal Gravimetric Analysis. Thermal gravimetric analyses were made for both electrically insulative and electrically conductive adhesives to evaluate their comparative temperature stabilities. Pyrograms (TGA curves) showing percent weight loss versus temperature are given in Figures 40 through 48. A listing of the electrically insulative adhesives in order of decreasing thermal stabilities as derived from Figures 40 through 44 is as follows:

HYSOL 0151
CURED - 2 HOURS AT 60°C
SAMPLE WEIGHT - 9.60 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
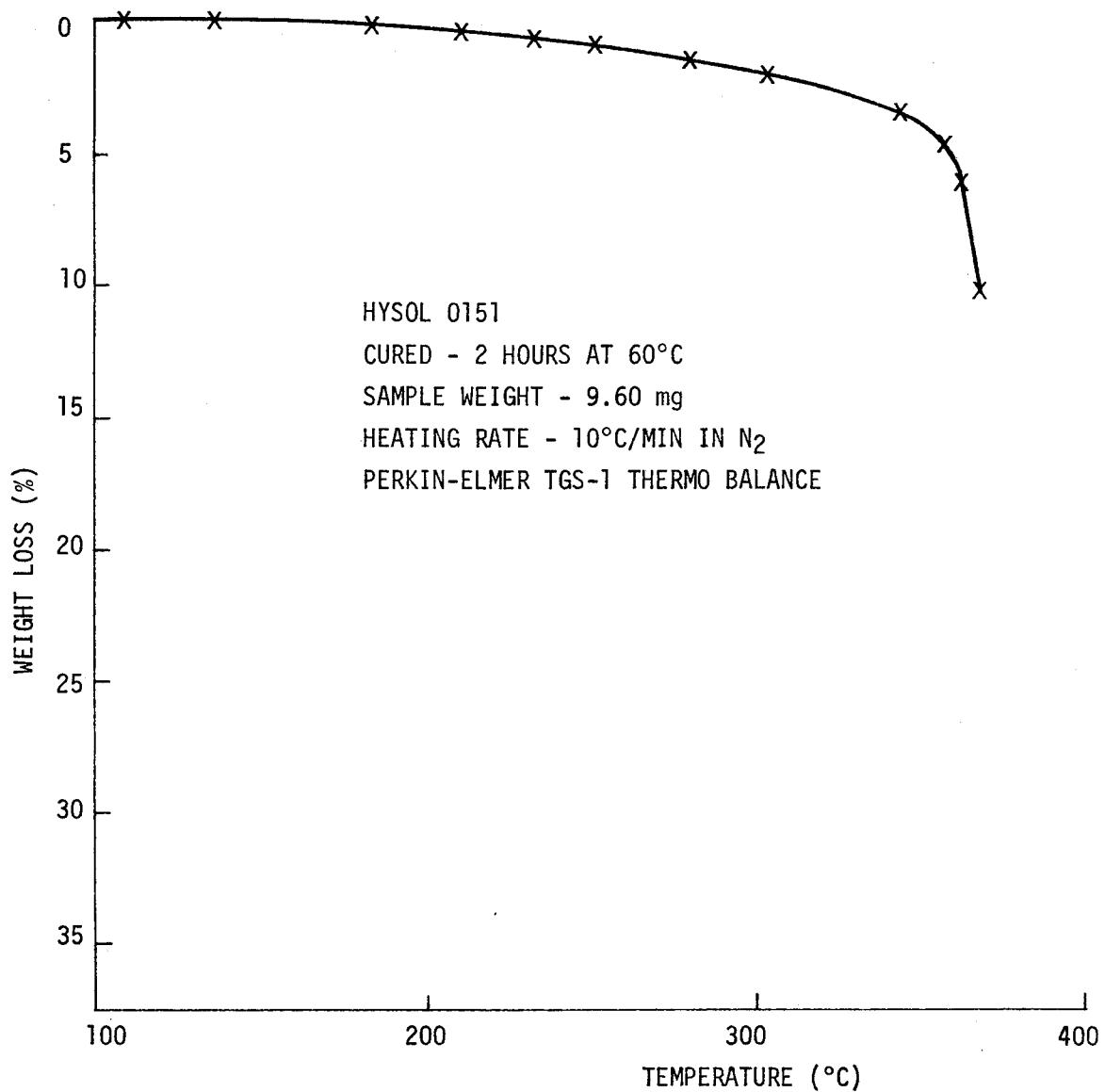
Figure 40.   TGA curve — Hysol 0151.

ABLEFILM 517
CURED - 30 MINUTES AT 150°C
SAMPLE WEIGHT - 4.552 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
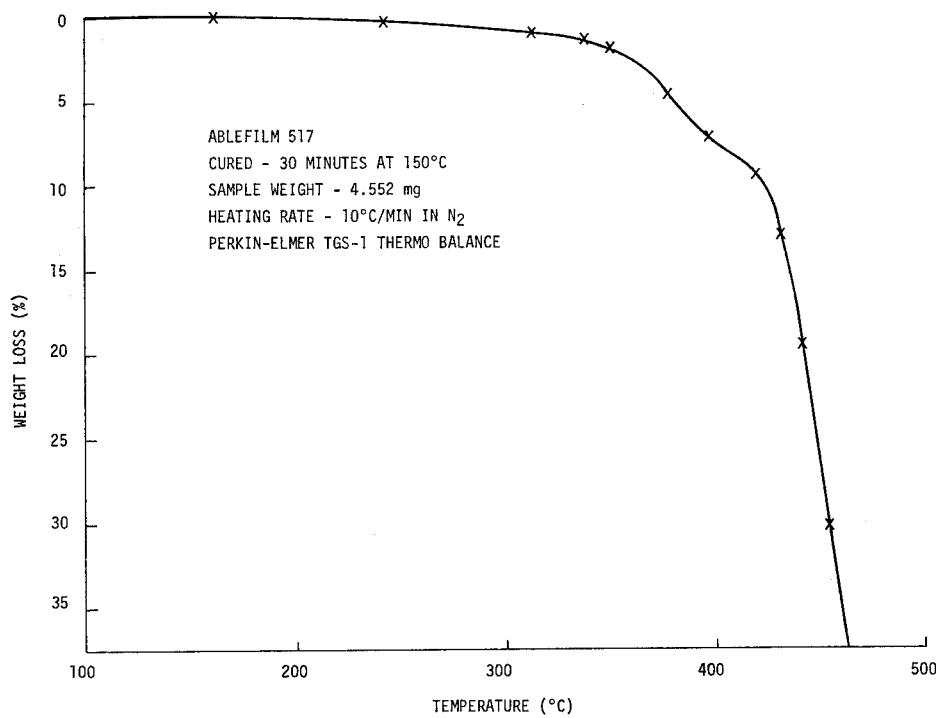
Figure 41. TGA curve — Ablefilm 517.

ECCOBOND 104
CURED - 3 HOURS AT 150°C
SAMPLE WEIGHT - 6.052 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
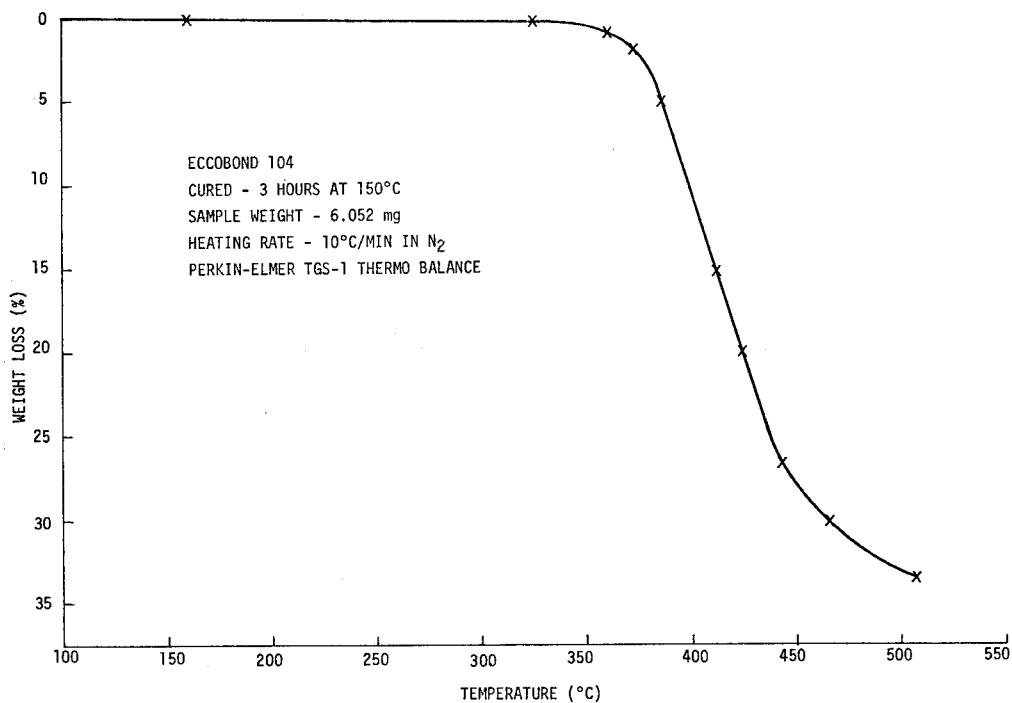
Figure 42. TGA curve — Eccobond 104.

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EPO-TEK H74
CURED - 40 MINUTES AT 100°C
SAMPLE WEIGHT - 7.420 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
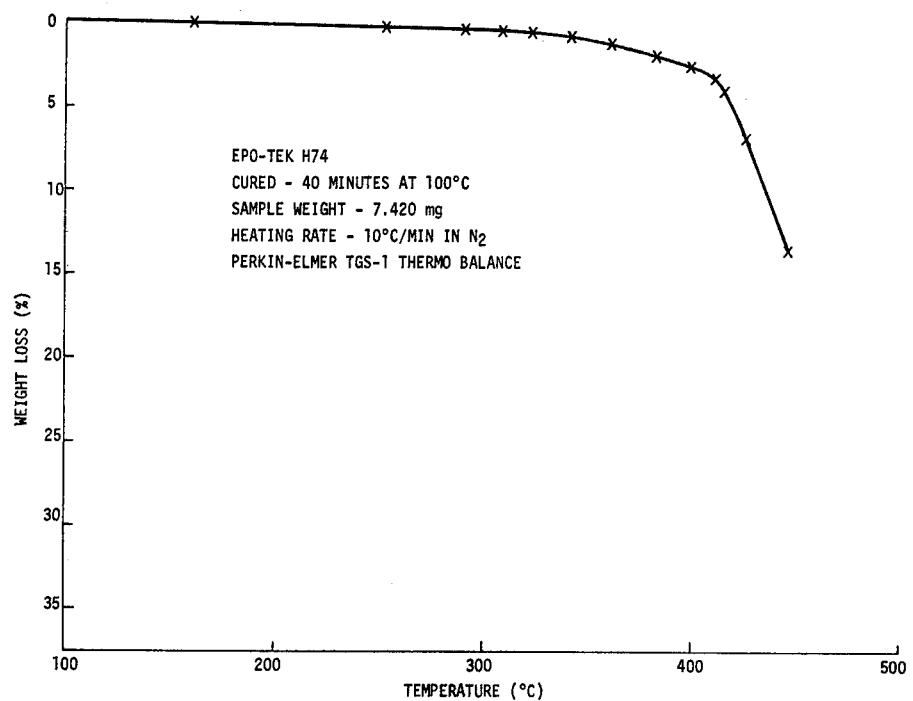
Figure 43. TGA curve — Epo-Tek H74.

EPO-TEK H61
CURED - 1 HOUR AT 150°C
SAMPLE WEIGHT - 20.52 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
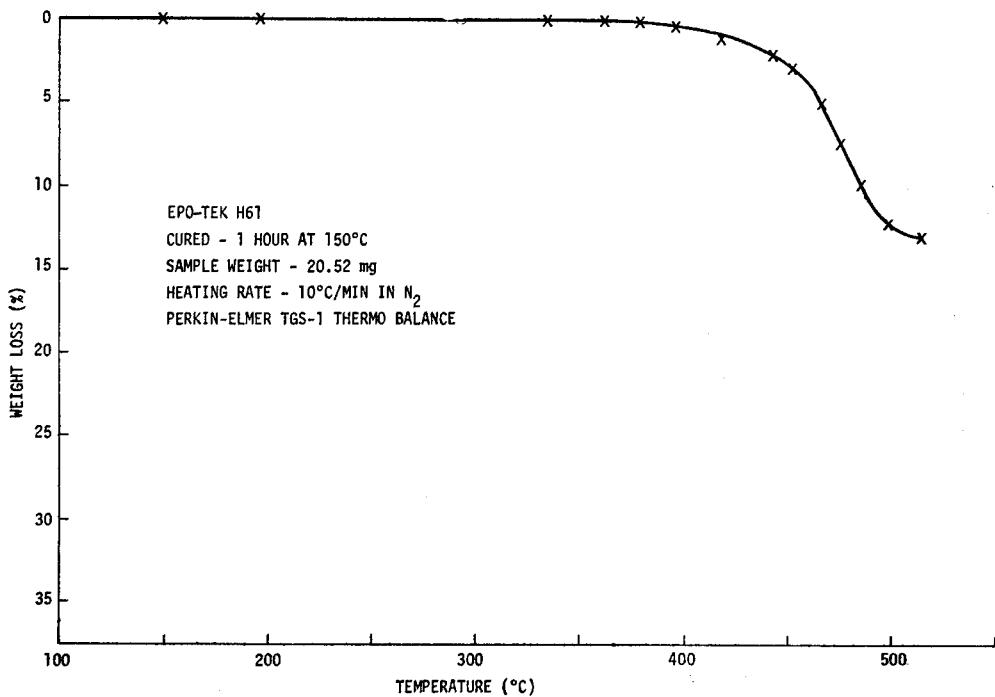
Figure 44. TGA curve — Epo-Tek H61.

41
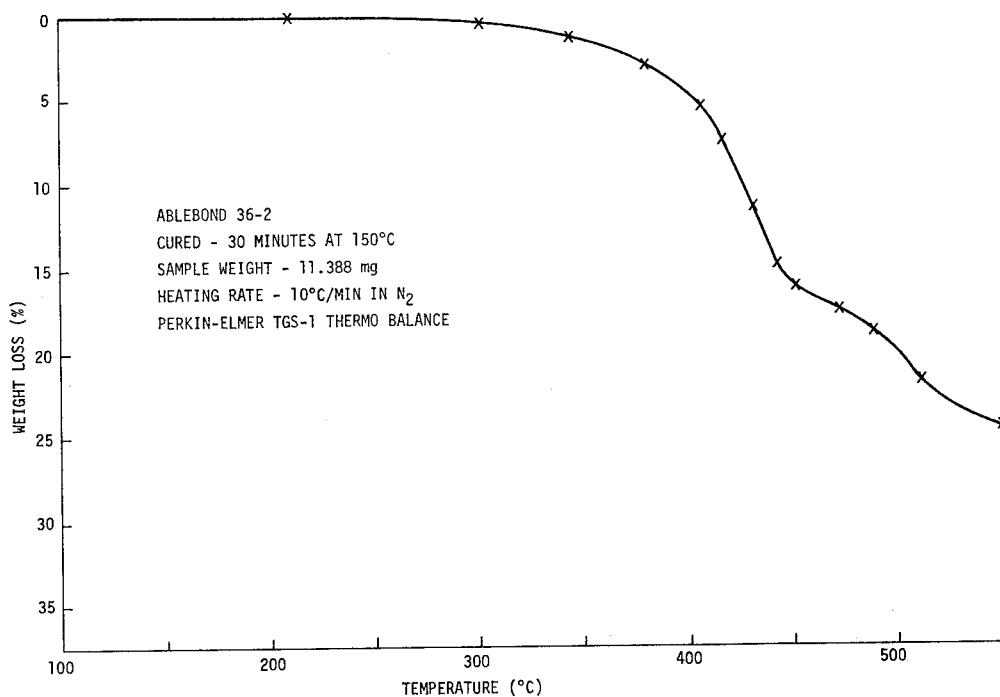
Figure 45. TGA curve — Ablebond 36-2.
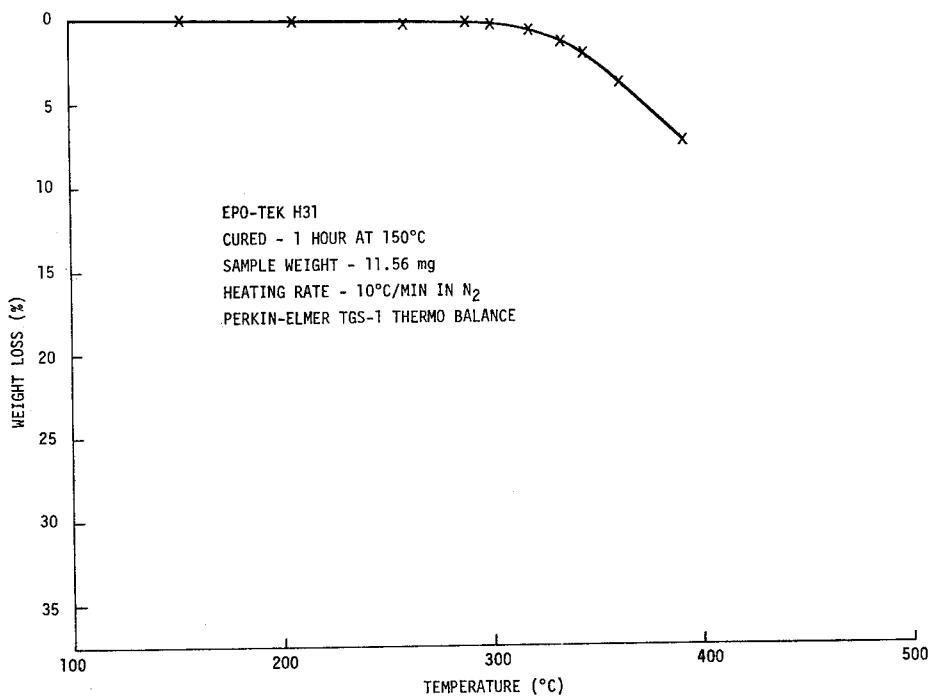
Figure 46. TGA curve — Epo-Tek H31.

42
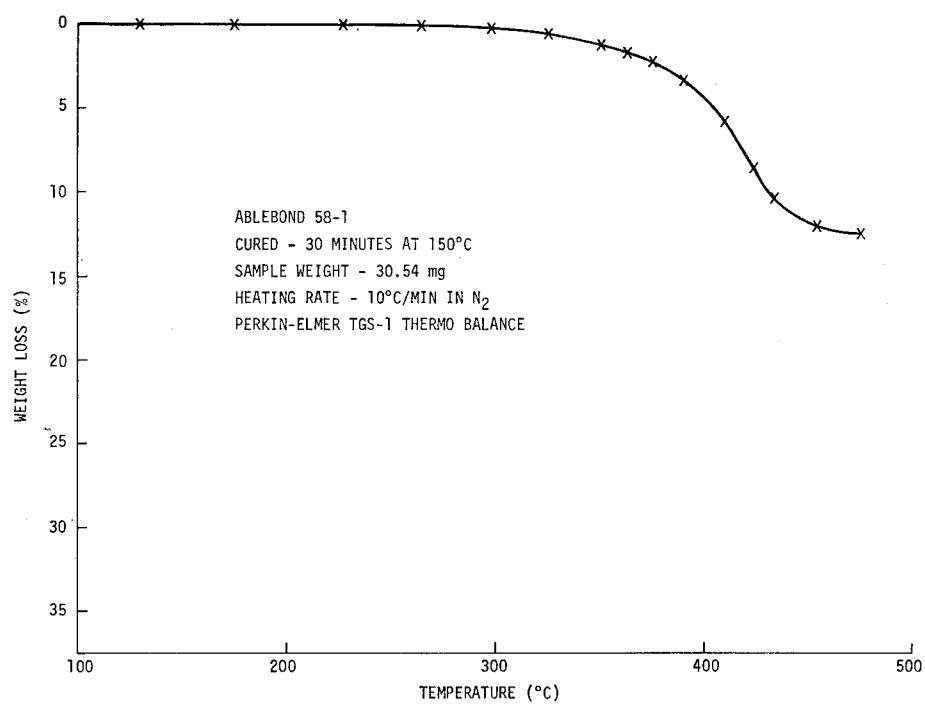
Figure 47. TGA curve — Ablebond 58-1.

ABLEBOND 58-1
CURED - 30 MINUTES AT 150°C
SAMPLE WEIGHT - 30.54 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE
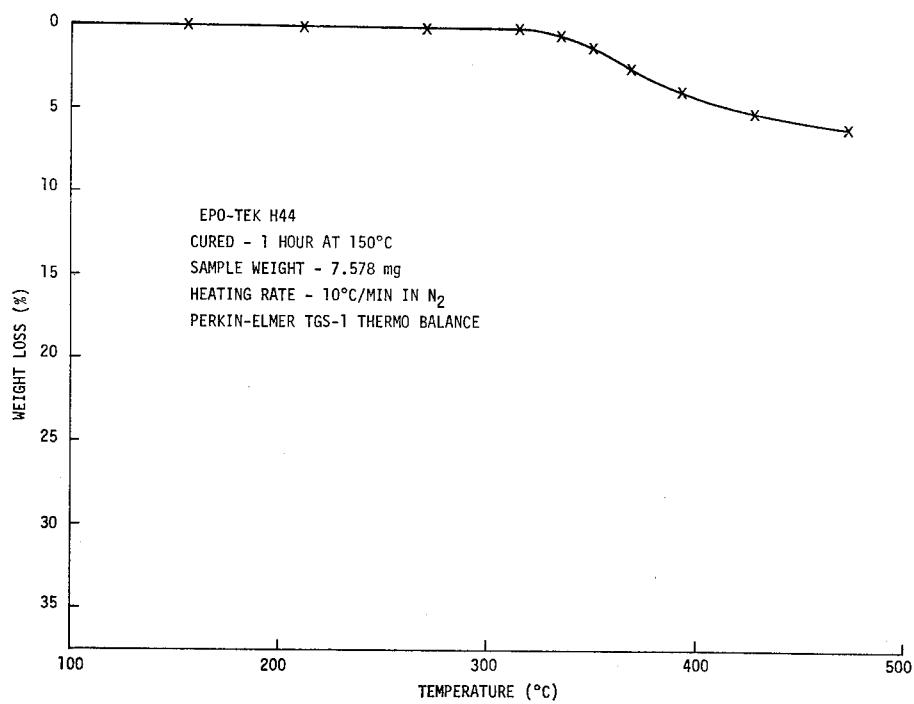
Figure 48. TGA curve — Epo-Tek H44.

EPO-TEK H44
CURED - 1 HOUR AT 150°C
SAMPLE WEIGHT - 7.578 mg
HEATING RATE - 10°C/MIN IN N_2
PERKIN-ELMER TGS-1 THERMO BALANCE

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1. Epo-Tek H61

2. Eccobond 104

3. Epo-Tek H74

4. Ablefilm 517

5. Hysol 0151

Hysol 0151 was definitely the least thermally stable of the adhesives tested. Its TGA curve indicates that it is at best marginal if exposed to a 150°C environment for a prolonged period of time. Comparison of the curves for the silver-filled adhesives, Ablebond 36-2 and Epo-Tek H31, shows that they are essentially coincident to about 320°C, a temperature which exceeds that to which hybrid circuits are exposed. This also is true for the gold-filled adhesives, Ablebond 58-1 and Epo-Tek H44. In fact, all of the curves for the metal-filled adhesives are essentially coincident over a temperature range exceeding that of practical interest for the present application.

Weight Loss After Cure. Although TGA curves provide important information on the thermal stabilities of adhesives, they do not provide weight-loss data at constant temperature as a function of time. Long-term outgassing data (1000 hr) at 150°C are desirable for initial qualification of adhesives and should be performed. However, a more practical short-term screening test is desirable to compare adhesives quickly. A test of this type would also be useful as a receiving inspection test. To investigate one possibility for such a test, the TGA apparatus was used at constant temperature (150°C), and weight losses were dynamically plotted over a 2-hr period for two different electrically insulative adhesives, Ablefilm 517 and Hysol 0151. Significant differences were found for these adhesives, as shown in Figure 49. This test therefore seems feasible as a method for rapidly and quantitatively assessing adhesives, but further work is required to determine its reproducibility and to establish the time required for the rate of loss to become constant.

Weight Loss During Cure. Weight loss during cure was determined for both electrically insulative and electrically conductive adhesives. The specimens were prepared by spreading the adhesives evenly into alumina cups (2.25 cm long by 1.80 cm wide by 0.15 cm deep). Approximately 0.5-gm samples of adhesive were used in all cases. A photograph of a specimen is shown in Figure 50. Measurements were made on an analytical balance capable of measuring to tenths of a milligram. The results are given in Table 3.
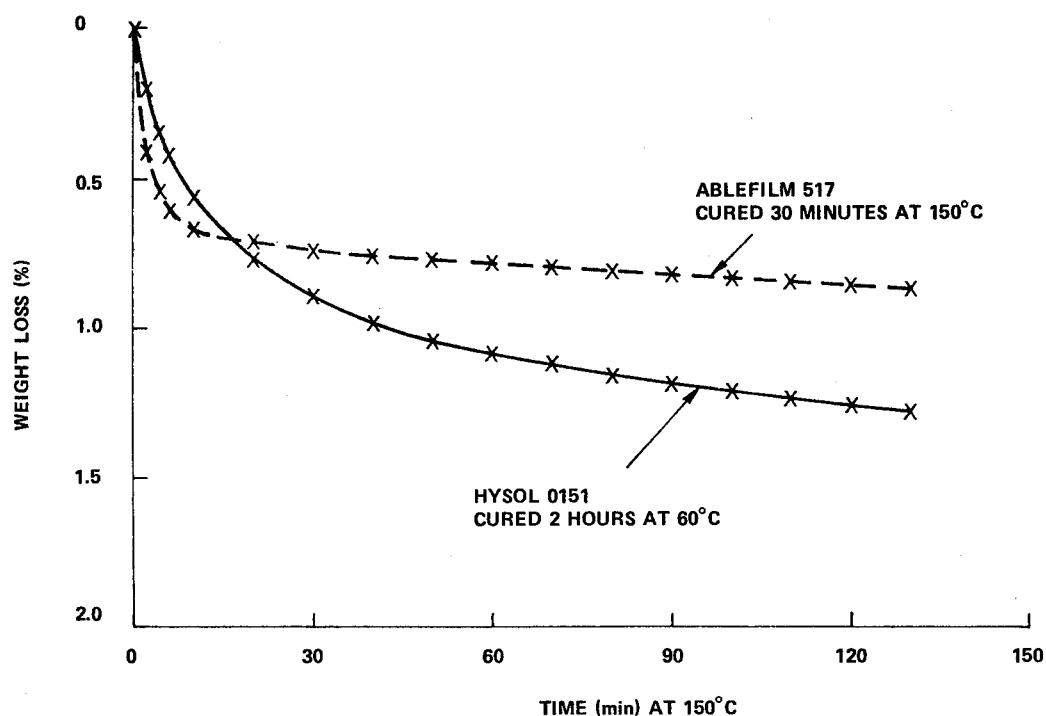
Figure 49. Weight loss after cure at constant temperature (150°C) as measured on TGA equipment.

Figure 50. Weight loss specimen.

TABLE 3. WEIGHT LOSS DURING CURE

Adhesive	Weight		Weight Loss	
	Before Cure (gm)	After Cure (gm)	(gm)	(percent)
Electrically Insulative				
Hysol 0151	0.5076	0.5066	0.0010	0.2
Ablefilm 517	0.2982	0.2934	0.0048	1.6
Eccobond 104	0.5066	0.5020	0.0046	0.9
Epo-Tek H74	0.5114	0.5097	0.0017	0.3
Epo-Tek H61	0.5288	0.5183	0.0105	2.0
Electrically Conductive				
Ablebond 36-2	0.5006	0.4865	0.0141	2.8
Epo-Tek H31	0.5066	0.4931	0.0135	2.7
Ablebond 58-1	0.5374	0.5257	0.0117	2.2
Epo-Tek H44	0.5293	0.5195	0.0098	1.9

It should be noted that the extent of weight loss of the adhesives during cure could not be correlated with the thermal stability of the adhesives after cure. A high initial weight loss during cure (in an open condition where volatiles can escape) may, in fact, be more desirable than any weight loss after cure (which would occur in a sealed package). Weight loss during cure is therefore considered meaningless as an indicator of adhesive reliability, except perhaps when the adhesives are used for lid sealing where there is a probability of the volatiles becoming entrapped in the package.

Chip Capacitor Bonding

Tests were made to evaluate the comparative reliability of mounting chip capacitors using electrically insulative adhesives (with flying leads for electrical connection) and using electrically conductive adhesives. The test substrates used were unglazed alumina 1.90-cm (0.75-in.) wide by 3.81-cm (1.50-in.) long with a single broken thick-film gold stripe 0.127-cm (50 mils)

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wide on them. A photograph of this test substrate is given in Figure 51. The capacitors used were manufactured by Monolithic Dielectrics, Inc., and consist of a ceramic dielectric with platinum electrodes and with silver terminals. Their physical dimensions are nominally 0.127-cm (50-mils) wide by 0.254-cm (100 mils) long by 0.102-cm (40-mils) thick. Bonds for the capacitors mounted with the electrically insulative adhesives were made ultrasonically using 0.0038-cm (1.5-mil) gold wire.

Sets of three test specimens, each comprised of four capacitors (a total of 12 capacitors), were prepared for each adhesive. The adhesives used were the same ones for which the corrosivity and weight loss evaluations were made, i.e., the electrically insulative adhesives Hysol 0151, Ablefilm 517, Eccobond 104, Epo-Tek H74 and Epo-Tek H61, and the electrically conductive adhesives Ablebond 36-2, Epo-Tek H31, Ablebond 58-1, and Epo-Tek H44. A photograph of a typical test specimen (for an electrically insulative adhesive) is shown in Figure 52.
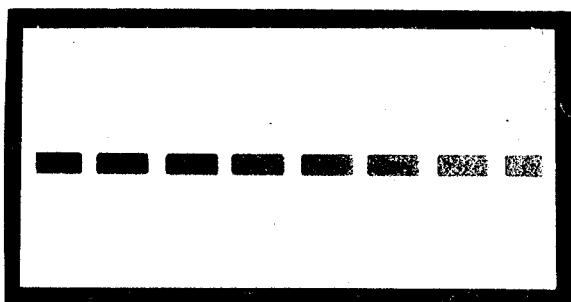

Figure 51. Test substrate for clip capacitor bonding evaluation.
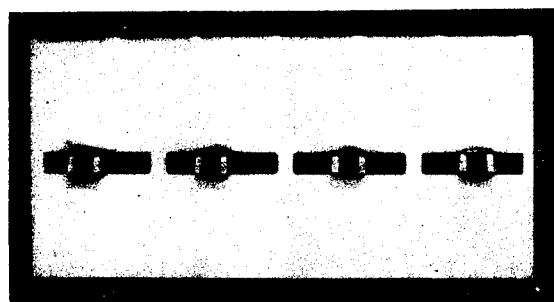
Figure 52. Typical chip capacitor bonding reliability test specimen.

Testing consisted of temperature cycling the specimens between -65°C and +150°C in accordance with MIL-STD-883 and visually inspecting then at 30X and measuring their capacitance. The specimens were temperature cycled for a total of 500 cycles. Visual inspection and capacitance measurements were made before cycling and after 10, 100, 200 and 500 temperature cycles. The test flow diagram is given in Figure 53. As shown in this diagram, capacitance measurements were made only at room temperature prior to temperature cycling and after 10 cycles and at room temperature, -65°C, and +150°C after 100, 200 and 500 cycles. Also, as shown in the flow diagram, for the electrically insulative adhesives, the bond strength was measured for one capacitor mounted with each adhesive at the end of 100 temperature cycles, for three
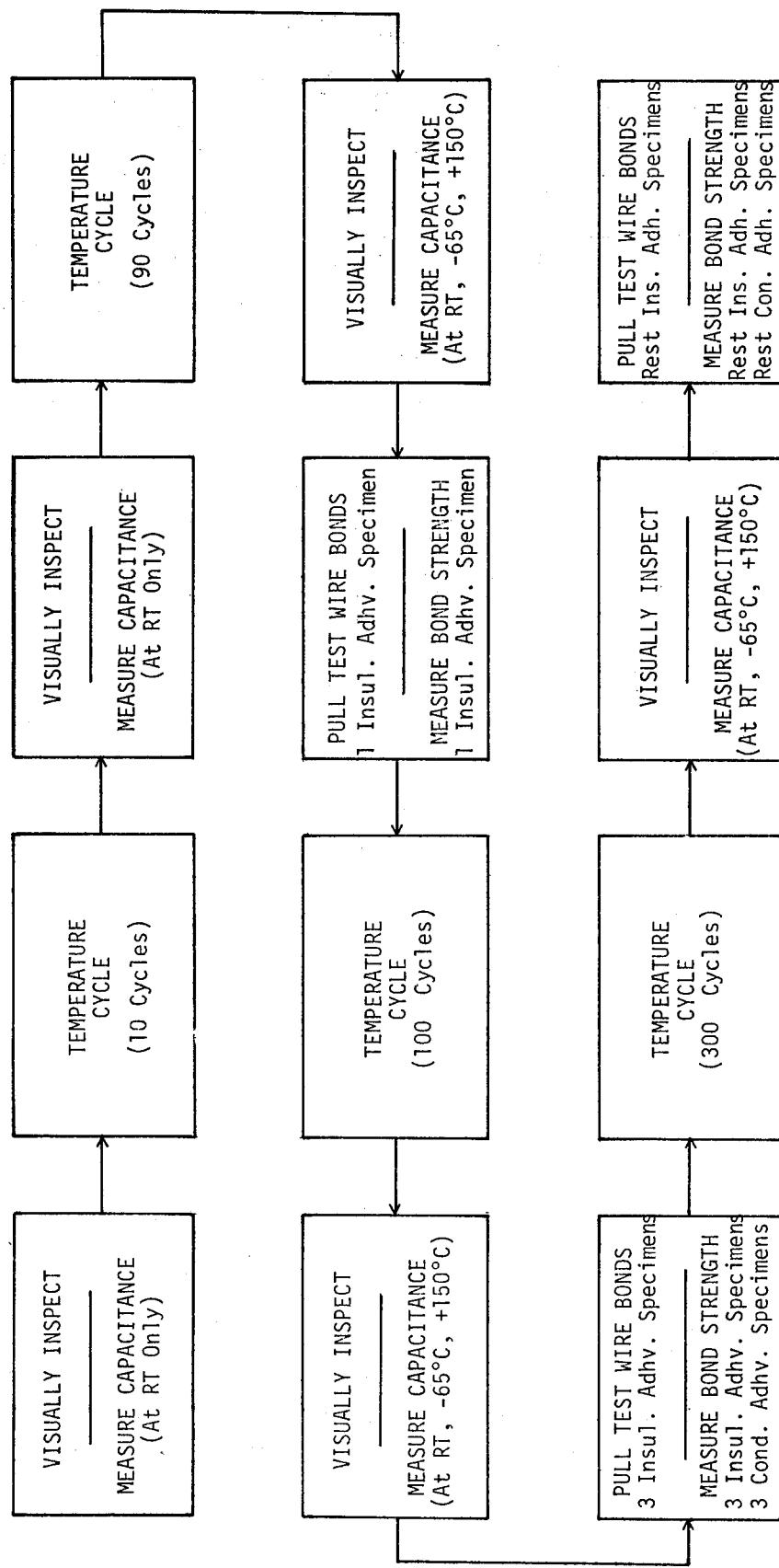
Figure 53. Chip capacitor bonding test flow diagram.

capacitors mounted with each adhesive at the end of 200 cycles, and for the rest (eight capacitors mounted with each adhesive) at the end of 500 cycles. Also, these specimens were pull-tested to determine the strength of the wire bonds. For the electrically conductive adhesives, the bond strength was measured for three capacitors mounted with each adhesive at the end of 200 temperature cycles and for the rest (nine capacitors mounted with each adhesive) at the end of 500 cycles.

Because of the size of the chip capacitors used in this investigation (compared with the size of the silicone die used for the adhesive bond strength tests) and the fact that in this case it was desired to test the bonds to failure, a tester of much greater shear force capability than that used for measuring the bond strengths of the adhesives was required. To meet this requirement, the tester shown in Figure 54 was assembled, and a fixture to hold the specimens was designed and fabricated. This tester can deliver approximately 445 N (100 lbf) or approximately 1.38×10^8 N/m^2 (20 000 psi) for the 0.127- by 0.254-cm (50- by 100-mil) capacitors used.

Visual inspection at 30X did not show any evidence of degradation of any of the adhesives until after 500 temperature cycles. After 500 cycles, it was observed that some cracking of the adhesive had occurred for Eccobond 104 and that Hysol 0151 had cracked in contours around all of the capacitors. This occurred sometime during the last 300 cycles (between inspection at 200 cycles and at 500 cycles). The cracking for Eccobond 104 varies from none to slight for different capacitors; however, for Hysol 0151, while the cracking was worse in some cases than others, it occurred for all capacitors. All other electrically insulative adhesives and all electrically conductive adhesives showed no visual evidence of cracking or degradation.

Figure 54. Chip capacitor bond strength tester.

Capacitance measurements at room temperature, at -65°C, and at +150°C did not indicate any evidence of catastrophic failures of any of the adhesives, or even of any substantial change in the capacitance values that would affect the performance of circuits in which the capacitors were used. The room-temperature measurements showed that in all cases the average values of the capacitance of the capacitors mounted with electrically insulative adhesives, and wire bonded, increased over their original values after temperature cycling and that in all cases the average values of the capacitance of the capacitors mounted with electrically conductive adhesives decreased.

After 200 cycles, the average values of the capacitors mounted with the various electrically insulative adhesives (except those mounted with Hysol 0151) had increased by 0.5 percent or less. Those mounted with Hysol 0151 had increased by a little over 2 percent. However, in this case, by far the major part of the change occurred during the first 10 cycles, indicating that for Hysol 0151 there is an initial annealing or some sort of adjustment occurring. Perhaps this is due to further curing of the adhesive during the hot portion of the temperature cycles. After 500 cycles, the average values of the capacitors mounted with Hysol 0151 had increased by about 3 percent, while the average value of those mounted with the other electrically insulative adhesives had increased by from 1 to 1.5 percent.

After 200 cycles, the average values of the capacitors mounted with the Epo-Tek conductive adhesives had decreased by 0.5 percent or less, whereas those mounted with the Ablestik adhesives had decreased by 0.75 to 1 percent. After 500 cycles, the average values of the capacitors mounted with the Epo-Tek conductive adhesives had decreased by about 0.6 percent, while the average values of those mounted with the Ablestik conductive adhesives had decreased by a little over 1 percent.

Results of the bond strength measurements are given in Tables 4 and 5. For the electrically insulative adhesives, results are given both as the total shear force (Table 4) and as the equivalent force per area derived from the dimensions of the specific capacitors used (Table 5). Since the effective bond area is not known for the electrically conductive adhesives, results are given as total shear force only. For these adhesives, the bond area is approximately one-third to one-fourth of the total area of the capacitor.

A comparison of these data indicates that temperature cycling has not substantially degraded the bond strengths of any of the adhesives. Ablefilm 517 had an appreciably lower bond strength than any other electrically insulative adhesive tested. The Ablestik electrically conductive adhesives had substantially higher bond strengths than the Epo-Tek electrically conductive adhesives.

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TABLE 4. CHIP CAPACITOR BOND STRENGTHS (SHEAR FORCE)

Adhesive	After 100 Cycles[a] (N)	(lb)	After 200 Cycles[b] (N)	(lb)	After 500 Cycles[c] (N)	(lb)
Electrically Insulative						
Hysol 0151	71.2	16.0	83.0	18.7	56.2	12.6
Ablefilm 517	26.7	6.0	13.3	3.0	35.6	8.0
Eccobond 104	100	22.5	108	24.3	153	34.4
Epo-Tek H74[d]	>89	>20	111	25.0	142	31.9
Epo-Tek H61[e]	142	32.0	157	35.3	147	32.9
Electrically Conductive						
Ablebond 36-2			36.0	8.1	24.0	5.4
Epo-Tek H31			10.8	2.4	9.9	2.2
Ablebond 58-1			42.3	9.5	27.8	6.3
Epo-Tek H44			220.8	4.7	16.0	3.6

a. Results are for one capacitor only.
b. Results are for three capacitors.
c. Results are for eight capacitors for the electrically insulative adhesives and for nine capacitors for the electrically conductive adhesives.
d. Epo-Tek H74 was not tested to failure after 100 cycles.
e. Bonds did not fail; capacitors fractured.

TABLE 5. CHIP CAPACITOR BOND STRENGTHS (FORCE PER AREA)

Adhesive	After 100 Cycles[a]		After 200 Cycles[b]		After 500 Cycles[c]	
	(N/m^2)	(psi)	(N/m^2)	(psi)	(N/m^2)	(psi)
Electrically Insulative						
Hysol 0151	2.21×10^7	3200	2.57×10^7	3730	1.74×10^7	2530
Ablefilm 517	8.27×10^6	1200	4.14×10^6	600	1.10×10^7	1600
Eccobond 104	3.10×10^7	4500	3.36×10^7	4870	4.74×10^7	6880
Epo-Tek H74[d]	$>2.76 \times 10^7$	>4000	3.45×10^7	5000	4.40×10^7	6380
Epo-Tek H61[e]	4.41×10^7	6400	4.87×10^7	7070	4.54×10^7	6590

a. Results are for one capacitor only.

b. Results are for three capacitors.

c. Results are for eight capacitors.

d. Epo-Tek H74 was not tested to failure after 100 cycles.

e. Bonds did not fail; capacitors fractured.

Wire bond pull tests were made to determine the bond strength of the wires used with the electrically insulative adhesives. All wire bonds withstood the 10-gm limit of the tester.

The major conclusion reached from this investigation is that either method of mounting chip capacitors (i.e., using electrically insulative adhesives with wire bonds or electrically conductive adhesives) is reliable. Neither method resulted in bonds that were subject to catastrophic failure or even substantial fatigue or degradation after prolonged (500 cycles) temperature cycling between -65°C and +150°C. However, since the effective bond area is three or four times greater for the electrically insulative adhesives than it is for the electrically conductive adhesives, the total bond strength of the electrically insulative adhesives is substantially greater. Depending on the mechanical (shock and/or constant acceleration) environments that must be withstood, effective bond area certainly becomes an important factor that must be considered in selecting the appropriate method of mounting chip capacitors.

ORGANIC COATINGS EVALUATION

This study was directed to evaluating the chemical, physical, electrical, and thermal compatibility of selected organic coating materials with typical hybrid microcircuit devices and materials to assess the suitability of using them as protective coatings. The utility of such a coating would be to immobilize metal particles that may have become entrapped in a hybrid package so that they cannot move around under vibratory or high-g forces and short out conductor lines or devices. Such a coating also would serve as a shield or barrier, preventing other materials arising from routine handling during testing and lid sealing from contaminating the microcircuit surface.

Specific major tasks performed during this study were as follows:

1. A test specimen consisting of components and materials typical of those used in hybrid microcircuits was designed and a number of them were fabricated.

2. Specific coating materials were selected for evaluation from the general classes previously identified as worthy of consideration. These were high-purity (semiconductor-grade) silicones, polyimides, sputtered Teflon, and p-polyxylylenes (Parylenes).

3. Electronic device parameters to be measured to evaluate the materials were selected, and the required test equipment was set up.

4. Test specimens were coated with the candidate materials and visually examined and electrically tested to evaluate their effects.

A detailed discussion of this effort will now be given.

Test Specimen

Each test specimen consisted of three npn and three pnp transistors, two CMOS chips each containing three n-channel and p-channel pairs (inverters), three chip capacitors, and three resistors each of three different inks (1, 10, and 100 kΩ per square). The layout of the test specimen and identification of the components are shown in Figures 55 and 56, respectively. A photograph of a completed test specimen is given in Figure 57. The transistors were eutectically mounted using a gold silicon preform by heating the substrates to approximately 325°C on a stage and then scrubbing the transistors and pulsing the stage to about 420°C. The chip capacitors and CMOS devices were mounted using the electrically insulative adhesive Eccobond 104, which was cured for 3 hr at 150°C. All electrical connections were made ultrasonically using 0.0038-cm (1.5-mil) gold wire. A total of 37 test specimens were made.

The substrates used were 96-percent alumina obtained from American Lava (AlSiMag 614) with a surface finish of approximately 0.0004 cm (16 μin.) CLA. Their physical dimensions were 5.08-cm (2-in.) square by 0.152-cm (0.060-in.) thick. The conductor metallization was thick-film gold (EMCA 3065). The thick-film resistors were made using 1-, 10-, and 100-kΩ-per-square Firon high-stability inks obtained from Electro Materials Corporation. As noted in Figure 56, 2N2222A and 2N2907A general-purpose amplifier chip transistors were used. These transistors were obtained from Motorola and have glassivated surfaces. The CMOS devices were triple inverters (14007A); these devices also were obtained from Motorola and also have glassivated surfaces. The capacitors used were manufactured by Monolithic Dielectrics, Inc., have gold terminals, and are approximately 0.254-cm (100-mils) long by 0.172-cm (50-mils) wide by 0.086-cm (25-mils) thick.

Selected Organic Coatings

Originally the coatings selected for evaluation included Parylene N and Parylene C; however, it was learned that these coatings were being evaluated by another contractor so they were deleted from the list. The coatings finally selected for evaluation were the following:
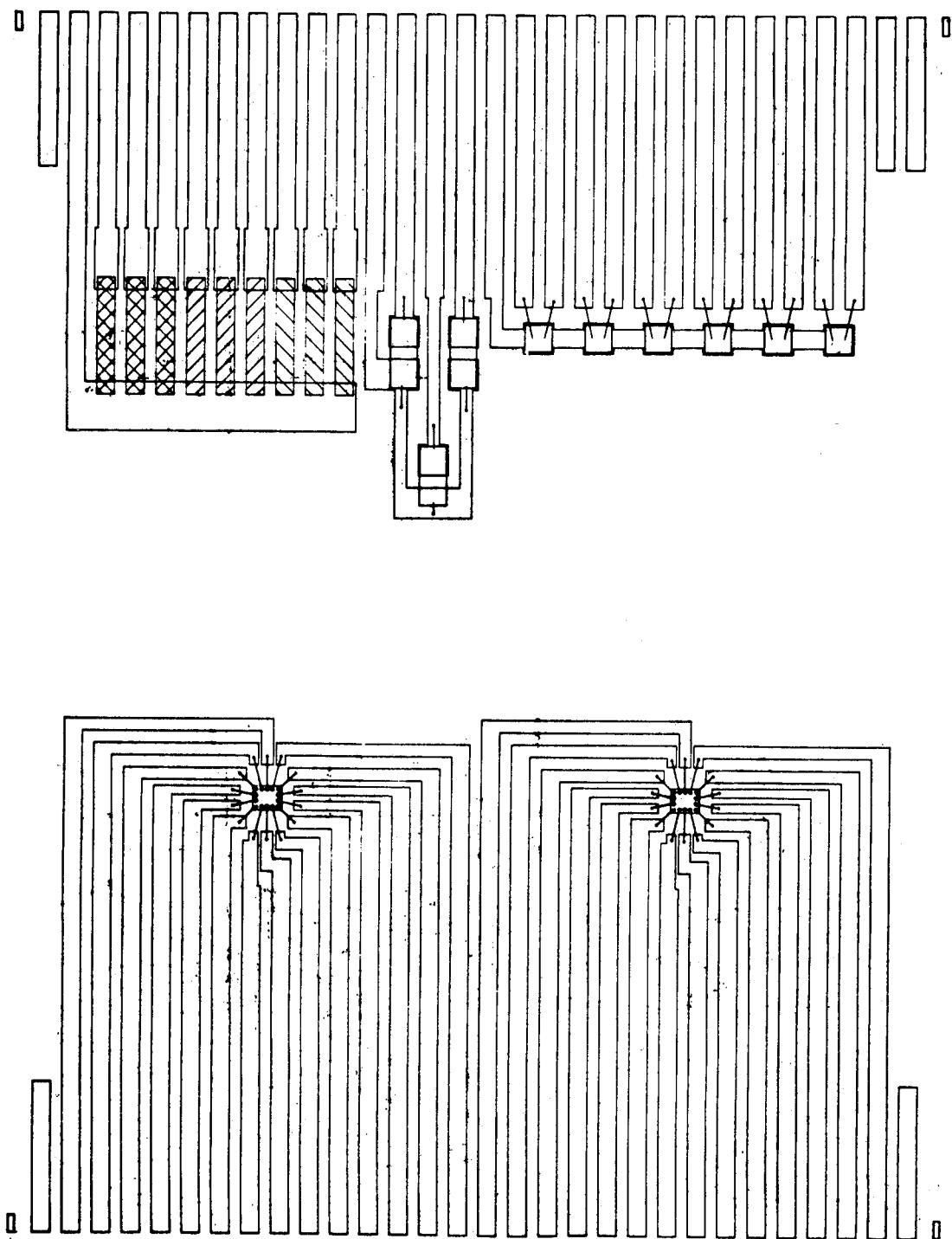
Figure 55. Layout of test specimen for evaluation of organic coatings.

55
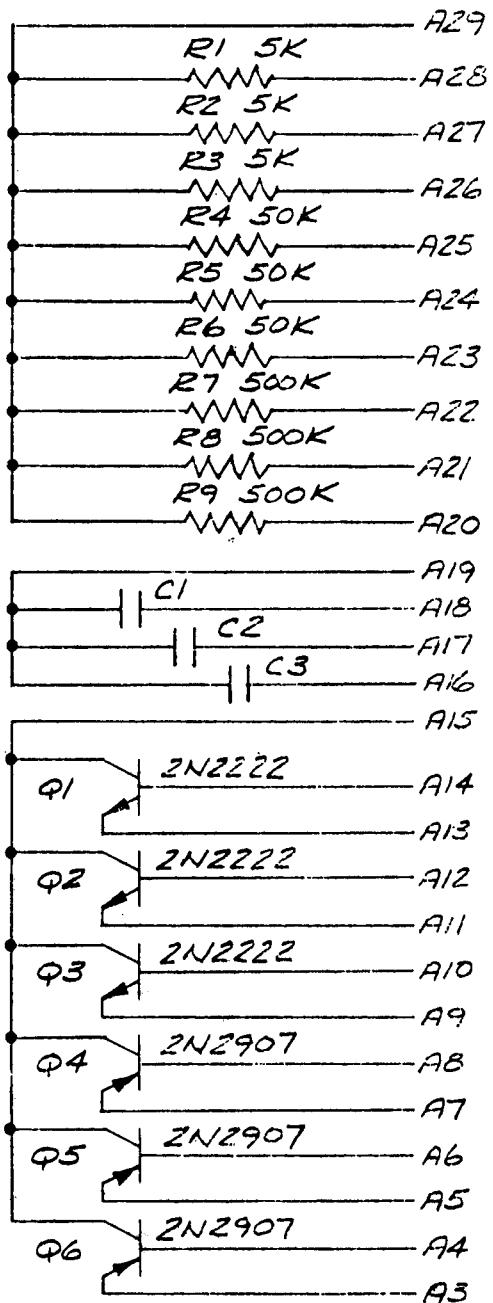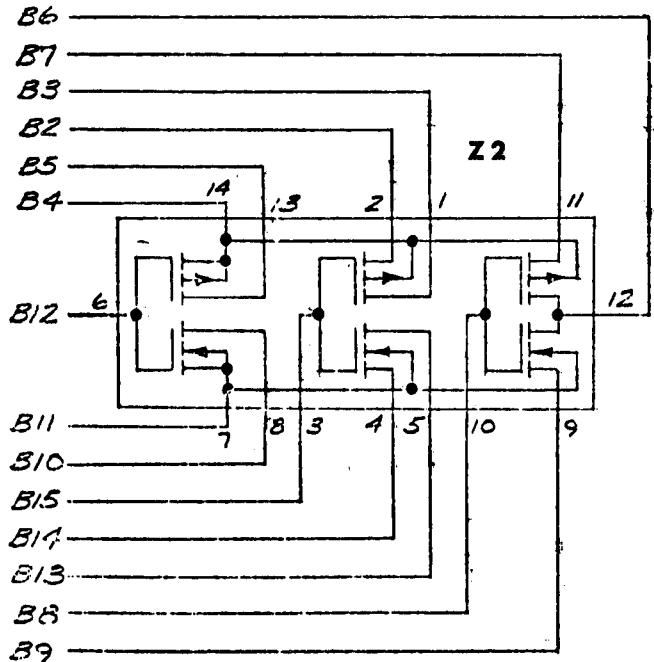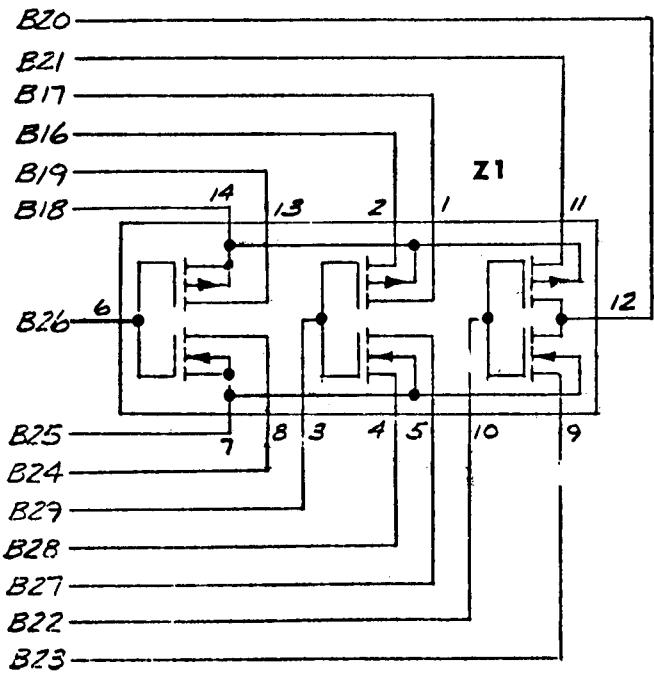
Figure 56. Identification of components on test specimen.

56
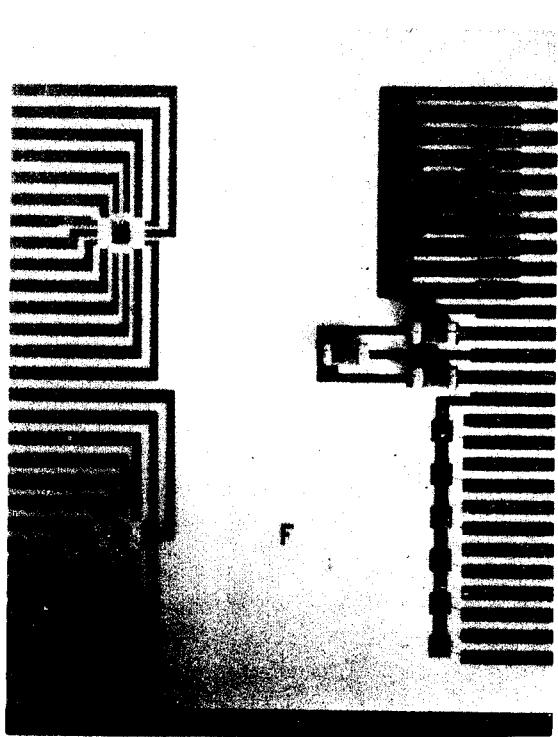
Figure 57. Completed test speci-
men for coatings evaluation.

1. Sputtered Teflon

2. Dow Corning R-6101

3. Dow Corning 649

4. Dow Corning XJR-90-702

5. DuPont Pyre-ML

6. General Electric EJC-245

The number of coatings selected was somewhat limited by the fact that the required curing temperature could not exceed 150°C. However, the preceding list represents all the general classes of coatings (excluding Parylene) previously identified as worth considering for the present application. DuPont Pyre-ML is a polyimide and the others (except, of course, the sputtered Teflon) are high-purity silicones. The silicones range from rigid to a soft, gel-like material. Dow Corning 649 is a rigid material, Dow Corning R-6101 and General Electric EJC-245 are flexible, elastomeric silicones, and Dow Corning XJR-90-702 is a gel. The curing schedules used were as follows:

DuPont Pyre-ML — Air-dry overnight at room temperature
        Cure — 30 min at 50°C
             — 30 min at 100°C
             — 2 hr at 150°C

Dow Corning R-6101 — Air-dry 1 hr at room temperature
        Cure — 1 hr at 70°C
             — 2 hr at 150°C

Dow Corning 649 — Air-dry 30 min at room temperature
        Cure — 30 min at 110°C
             — 12 hr at 125°C

Dow Corning XJR-90-702 — Air-dry 1 hr at room temperature
Cure — 2 hr at 150°C

General Electric EJC-245 — Air-dry 1 hr at room temperature
Cure — 90 min at 150°C

Critical Electrical Parameters and Test Equipment

All of the electrical parameters that could be measured for the various components were considered but, to keep the testing required reasonable, only those believed to be most sensitive to the effects of coating materials were selected for measurement. These were as follows:

1. Thick-Film Resistors   Resistance

2. Chip Capacitors   Capacitance at 1000 Hz

3. Transistors   Collector-Base Reverse Leakage Current (I_{CBO})

                                  dc Base Current (I_B)

                                  Forward Emitter-Base Voltage (V_{BE})

4. CMOS Devices   Quiescent Device Leakage Currents (I_{QL}, I_{QH})

                                  Output Voltages (V_{OL}, V_{OH}) at Rated Noise Immunity Voltage

The quiescent device leakage currents I_{QL} and I_{QH} were measured with all three inverters in parallel. I_{QL} was determined with the gate-to-source voltage (V_{GS}) equal to zero, I_{QH} with the gate-to-source voltage at 10 V.

The test equipment required to measure these parameters was set up. An FET Volt-Ohm-Meter with a low range of 30 nA full scale was used for measuring the currents. Gate voltages were supplied by a Harrison precision power supply capable of ±1 mV precision. Voltages and resistances were measured with a Dana 5500 digital meter, and a Boonton Model 74C-58 capacitance bridge accurate to 0.25 percent from 100 to 1000 pF was used to measure the capacitances.

Also, a switching unit called an input/output interface multiplexer was designed and fabricated so that the components could be selected for testing by simply setting switches in a particular configuration. A photograph of the test setup is given in Figure 58. A closeup of the input/output interface multiplexer is given in Figure 59.

Evaluation of Coating Effects

The procedure used to evaluate the various coatings was as follows:

1. Test specimens were initially visually inspected and electrically tested.

2. These specimens were then subjected to a burn-in consisting of 168 hr at 125°C with power applied to the various devices and 168 hr at 125°C without power applied. All test specimens were again visually inspected and electrically tested.

3. The best test specimens were selected and grouped into six sets, each containing at least 12 npn and 12 pnp transistors, four CMOS chips with 12 n-channel and p-channel pairs, 12 chip capacitors, and 12 resistors each of three different resistance ranges (5, 50, and 500 kΩ).

4. Each set of test specimens was coated with one of the six selected coating materials and visually inspected and electrically tested.

5. These sets were then temperature cycled between -65°C and +150°C for a total of 25 times and again visually inspected and electrically tested.

Before the results obtained are discussed, criteria will be established for judging whether the various electronic components are good, and comments will be made concerning the application of the various coating materials.

For the CMOS devices, with the supply voltage V_{DD} at 10 V, the values of the quiescent device leakage currents I_{QL} and I_{QH} with all three inverters in parallel should be in the low nanoamp range (from 1 to 100 nA). However, devices are still usable with values of I_{QL} and I_{QH} of the order of a few micro-amps, provided that power dissipation is not a prime consideration. The noise threshold gate voltages V_{NL} and V_{NH} should be approximately 30 percent of the value of V_{DD}. The corresponding output voltages V_{OL} and V_{OH} then should
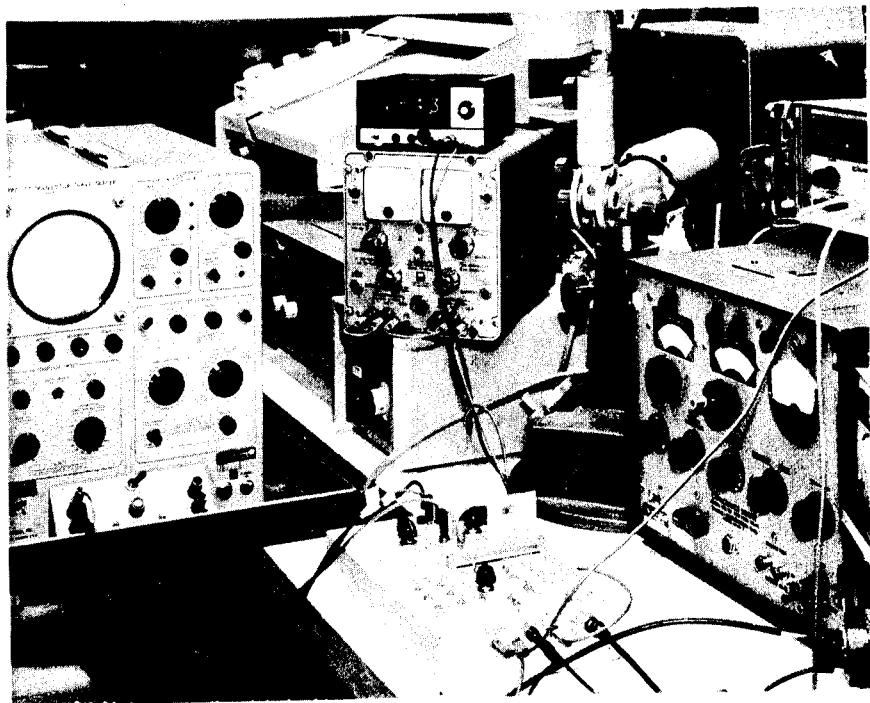
Figure 58. Coatings evaluation test equipment setup.
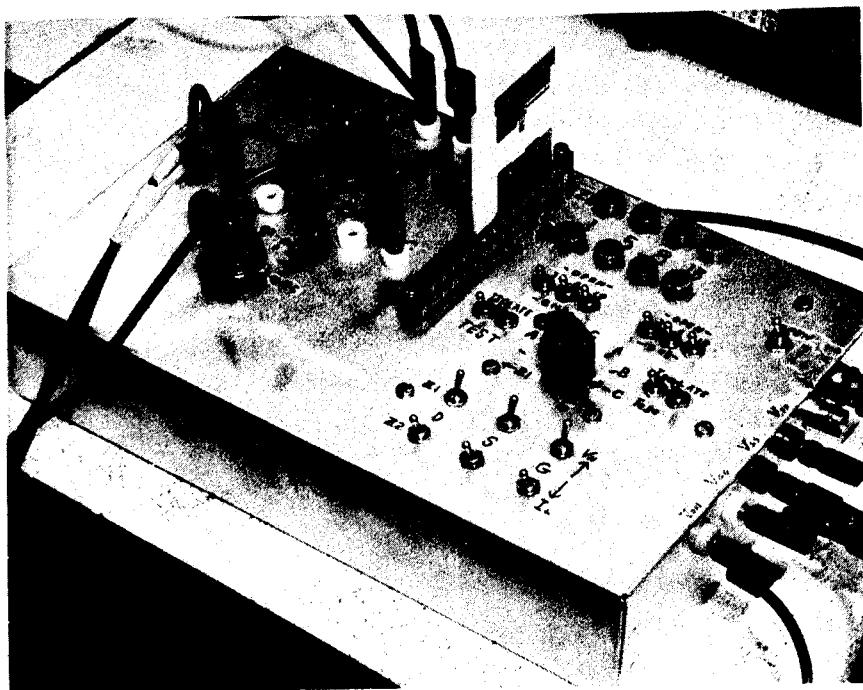
Figure 59. Input/output interface multiplexer.

differ from 10 V and 0 V, respectively, by less than 1 V. For this study, gate input voltages of 3 and 7 V were chosen as representative values for the noise immunity input voltages. For the transistors, the collector-base leakage current I_{CBO} should not be greater than 10 nA at 60 V reverse bias, and the dc base current I_B should not be greater than 20 μA for a collector current I_C of 1 mA if a minimum gain of 50 is required. Also, the forward emitter-base voltage V_{BE} should be between 0.6 and 0.7 V. Specific values of the capacitors and resistors are unimportant, but they should not change by more than 1 percent in value during the tests.

Except for the Teflon coating which was sputtered, all the coating materials were sprayed. Spraying was done using a Paasche air brush with a conventional tip at low pressure from a distance of approximately 15 to 20 cm (6 to 8 in.) to attempt to avoid damaging the test specimens. Contacts at the edge of the board were masked with Teflon tape to avoid contaminating them. Since the materials were too viscous for spraying as received, they were diluted as necessary with a solvent recommended by the manufacturer. Viscosities and approximate mix ratios for the various coatings were as follows:

Coating	Viscosity (cP)	Mix Ratio
DuPont Pyre-ML	600 to 1000	1 part Pyre-ML 4 parts dimethyl-formamide
Dow Corning R-6101	4500 to 9000	2 parts R-6101 3 parts Toluene
Dow Corning 649	100 to 150	3 parts 649 1 part Toluene
Dow Corning XJR-90-702	380	1 part XJR-90-702 1 part Toluene
General Electric EJC-245	4000	1 part EJC-245 1 part Toluene

Results obtained during the evaluation study will now be discussed. Initial visual inspection at 30X indicated that all 37 test specimens were assembled properly. Initial electrical testing showed that 24 of the 74 CMOS chips, 16 of the 111 npn transistors, and 17 of the 111 pnp transistors were defective (i.e., did not meet the criteria previously listed for a good device). Also, one capacitor was found to be open. Visual reinspection revealed that

the right-hand wire had been broken on this capacitor. After burn-in consisting of 168 hr at 125°C with power applied and 168 hr at 125°C without power applied, visual inspection at 30X did not reveal any additional defects. However, electrical testing showed that only 28 of the CMOS chips were good, 11 npn and 10 pnp transistors were defective, and nothing of significance had happened to the chip capacitors and thick-film resistors.

Of the CMOS chips, only 18 had I_{QL} and I_{QH} in the nanoamp range. Since 24 CMOS chips were required to provide 12 CMOS inverters (each chip contains three inverters) for each of the six coatings to be tested, six CMOS chips with I_{QL} and/or I_{QH} in the low microamp range had to be used. Consequently, six sets of test specimens were carefully selected to ensure that each set contained at least 12 good devices of each type (i.e., n-channel and p-channel pairs, npn transistors, pnp transistors, capacitors, and resistors of three different values).

Each of these sets was coated with one of the six selected coatings as follows:

Set 1 (comprised of test specimens 6, 8, 14, and 16) — Sputtered Teflon

Set 2 (comprised of test specimens 9, 10, 11, 24, and 27) — Dow Corning R-6101

Set 3 (comprised of test specimens 5, 13, 15, 30, and 32) — Dow Corning 649

Set 4 (comprised of test specimens 2, 3, 19, 23, and 28) — Dow Corning XJR-90-702

Set 5 (comprised of test specimens 18, 20, 29, and 31) — DuPont Pyre-ML

Set 6 (comprised of test specimens 4, 21, 22, 33, and 35) — General Electric EJC-245

The results observed after coating were as follows:

1. Dow Corning XJR-90-702 failed to cure at the recommended cure schedule. An effort to cure it at an extended schedule also was unsuccessful. Consequently, no further testing was performed on this set.

2.   Although care was taken in spraying the coatings and in handling the test specimens during the coating process, it obviously was inadequate. The 0.0038-cm (1.5-mil) gold wires are very delicate and many of them were either mechanically damaged in handling or by the force of the spray used in applying the coatings.

3.   Electrical testing showed the following:

   a.   Sputtered Teflon — All CMOS devices and transistors were severely damaged after sputtering. For the npn transistors, both I_{CBO} and I_B were affected; for the pnp transistors, only I_B was affected.

   b.   Dow Corning R-6101 — No adverse effects were noted on any parameters of any components.

   c.   Dow Corning 649 — No adverse effects were noted.

   d.   Dow Corning XJR-90-702 — Coating material failed to cure, so electrical measurements were not made.

   e.   DuPont Pyre-ML — This coating did not adversely effect the transistors, chip capacitors, or thick-film resistors. However, unfortunately, nothing can be said as to its effect on CMOS devices since wires were shorted together for all of the CMOS devices because of the high spray pressure used in applying the coating material.

   f.   General Electric EJC-245 — I_{QL} and I_{QH} of one CMOS device (of the four tested) increased substantially; otherwise, no adverse effects were noted.

Finally, those sets coated with Dow Corning R-6101, Dow Corning 649, DuPont Pyre-ML, and General Electric EJC-245 (sets 2, 3, 5 and 6, respectively) were temperature cycled for a total of 25 times between -65°C and +150°C. The results observed after temperature cycling were as follows:

1.   Casual unaided visual inspection showed that the right silicone coating, Dow Corning 649, had cracked and separated from the substrate.

2.   Visual inspection at 30X showed that no test specimens had changed except those coated with Dow Corning 649. This coating not only had cracked and separated from the substrate, but also had pulled wires loose from the pads

on the CMOS devices and transistors. Photographs of test specimens coated with Dow Corning R-6101 and with Dow Corning 649 are given in Figures 60 and 61 to show the contrast between these coatings after temperature cycling.

3.   Test specimens coated with the remaining three materials and temperature cycled showed no electrical parameter changes. No conclusions can be drawn for DuPont Pyre-ML on CMOS devices because these devices were all damaged (wires shorted together) because of the spray pressure used in applying the coating material.

CONCLUSIONS

This preliminary study showed that both of the flexible silicones evaluated, Dow Corning R-6101 and General Electric EJC-245, were satisfactory for use as protective coatings for hybrid microcircuits. Also, it appears that DuPont Pyre-ML is a satisfactory coating material. However, further testing should be performed using a larger number of test specimens to obtain more statistically significant results, and these specimens should be subjected to MIL-STD-883 test conditions (in appropriate sequence) before a final decision on the suitability of these materials is made. Results also showed that sputtered Teflon and the rigid silicone, Dow Corning 649, are unsatisfactory for use as microcircuit coatings. For the sputtered Teflon, the transistors and CMOS devices were severely damaged during the sputtering process and this damage is assumed to result from secondary radiation. However, this problem possibly may be avoided by using newly introduced sputtering equipment with special cathodes which magnetically divert the charged particles from the substrate. Consequently, sputtered Teflon may still be a viable candidate coating. The rigid silicone, Dow Corning 649, is unusable because the stresses set up during temperature cycling cause it to crack, separate from the surface, and pull wires loose from the device pads. Unfortunately, the silicone gel, Dow Corning XJR-90-702, did not cure, so no conclusion can be given for it.
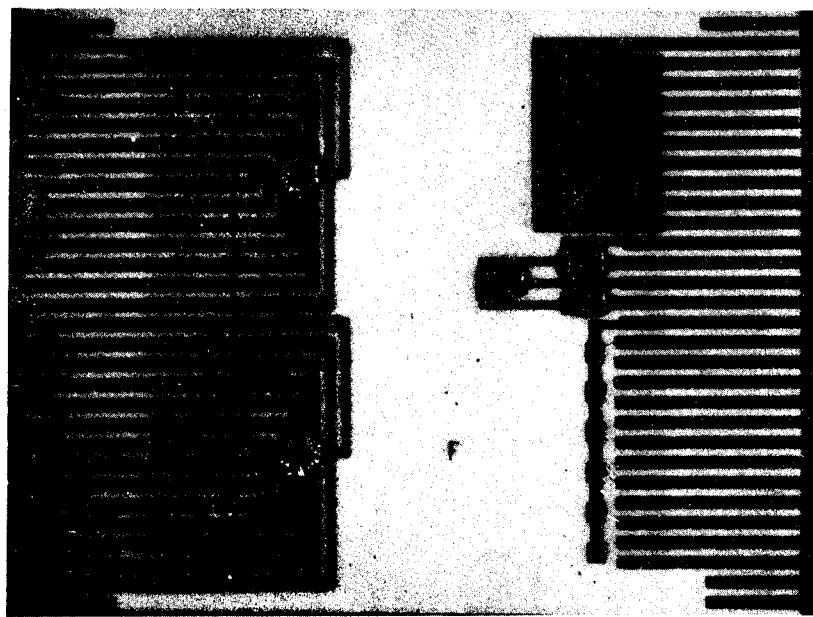
Figure 60. Test specimen coated with Dow Corning R-6101 after temperature cycling.
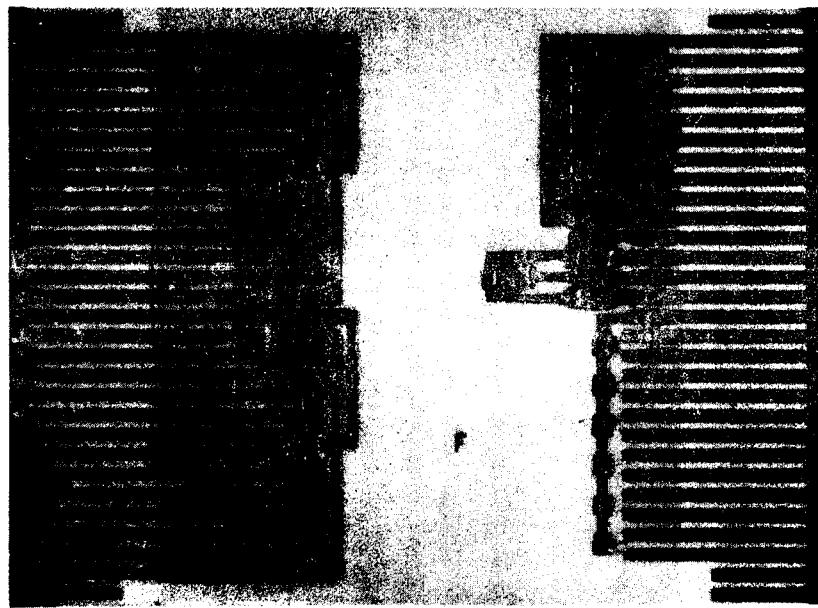
Figure 61. Test specimen coated with Dow Corning 649 after temperature cycling.

APPROVAL

DESIGN GUIDELINES FOR USE OF ADHESIVES AND ORGANIC COATINGS IN HYBRID MICROCIRCUITS

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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